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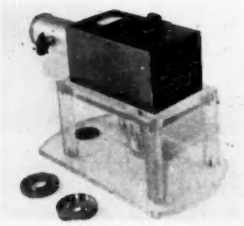

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Stress-Strain Relationships in Yarns Subjected to Rapid Impact Loading

Part IV: Transverse Impact Tests*

Jack C. Smith, Frank L. McCrackin, Herbert F. Schiefer, Walter K. Stone, and Kathryn M. Towne

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Abstract

If a textile yarn segment, clamped at each end, is impacted transversely at the midpoint, the stress-strain curve for this yarn can be obtained from measurements on a high speed photographic record of the yarn's motion. This paper describes the apparatus and procedure used. Stress-strain curves for high rates of straining, of the order 5000%/sec., obtained by this method are given for high tenacity nylon, Fortisan, and Fiberglas. Comparison with stress-strain data obtained at conventional rates shows that these materials have higher initial moduli, and that their stress-strain curves remain linear up to higher stress values, when the testing rate is high. The breaking tenacities are slightly greater and breaking elongation slightly smaller at these high test rates.

Introduction

In previous papers of this series [1, 5, 9] the behavior of textile yarns subjected to longitudinal impacts of order of magnitude 50 m./sec. was discussed. Equipment using high speed photography was described. A procedure for obtaining stress-strain curves at initial rates of straining of the order of 5000%/sec. (300,000%/min.) was given. The concept of a limiting breaking velocity, approximating the lowest velocity at which a textile yarn will rupture immediately upon tensile impact was introduced, and values of this characteristic quantity were given for several different yarns.

Equipment for studying the behavior of yarns impacted transversely at velocities of order of magnitude 50 m./sec. has now been constructed. This equipment is described here. A method of obtaining stress-strain curves from photographs of the successive configurations of a clamped yarn subjected to transverse impact is outlined. Stress-strain data obtained in this way are given for high tenacity yarns of nylon, Fortisan, and Fiberglas.

Apparatus

An assembly of the transverse impact equipment is shown in Figure 1. The yarn specimen is clamped to a rigid massive table A, on which a coordinate grid system is inscribed. Central transverse impact is made by a freely flying projectile which has been

* Part I appeared in TEXTILE RESEARCH JOURNAL **6**, 520 (1955); Part II, **6**, 529 (1955); Part III, **8**, 701 (1955). This paper was published by the *Journal of Research of the National Bureau of Standards* **57**, No. 2, 83 (1956).

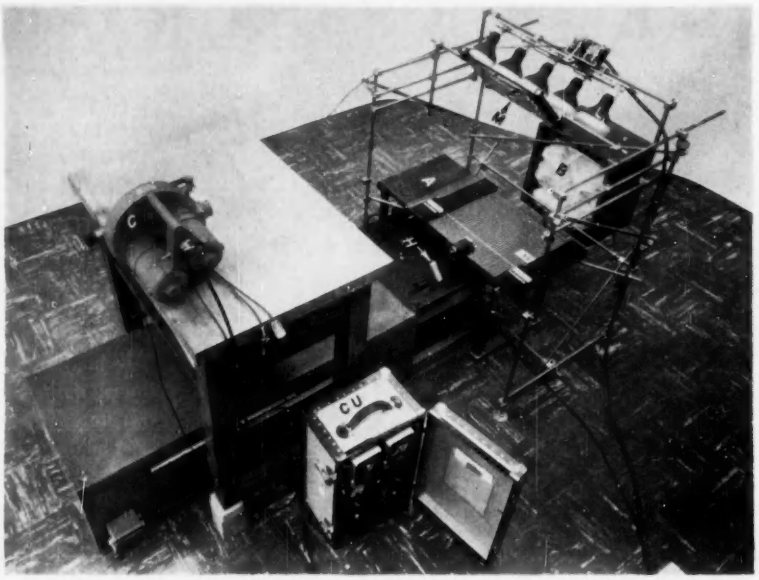

Fig. 1. Apparatus for impacting yarn specimens transversely. A table, H hammer, C camera, CU control unit, L lamps, M mirror, B catch box.

struck by a rapidly rotating hammer H. Apparatus for rotating and stopping the hammer is separate from the specimen table in order to avoid jarring.

The 6-in. hammer rotates under a powerful torque through an arc of 270° before striking. The force to rotate the hammer is applied at the surface of a 2-in. shaft by straps from four springs which can be extended up to 20-in. by a motor. At full extension the total tension in the four springs is 800 lb. The hammer is held in place by a latch which can be suddenly released by a solenoid. Projectile speeds have been measured as high as 70 m./sec.

Reflected images of the specimen after impact are photographed by the high speed camera C on the table shown. Either of two Fastax cameras capable of rates of 7000 or 14,000 pictures per second, respectively, was used for this purpose.

Other parts of the equipment shown in Figure 1 are the control unit CU which puts timing pips on the film and triggers the hammer when the camera is up to speed, the five 750 W flood lamps L for illuminating the specimen, the mirror M for reflecting the image of the specimen into the camera, and the box B for catching the projectile.

Figure 2 shows a close-up of the specimen, specimen table, projectile, hammer, and driving springs. The shapes which the specimen assumes after impact, as recorded by the camera, are shown in Figure 3 for a typical yarn specimen.

Analysis of the Data

When a yarn is struck transversely by a projectile traveling at a velocity V, a longitudinal strain wave [1] is propagated along the yarn with velocity C outward in each direction from the point of impact. (See curve a in Figure 4). In the strained region

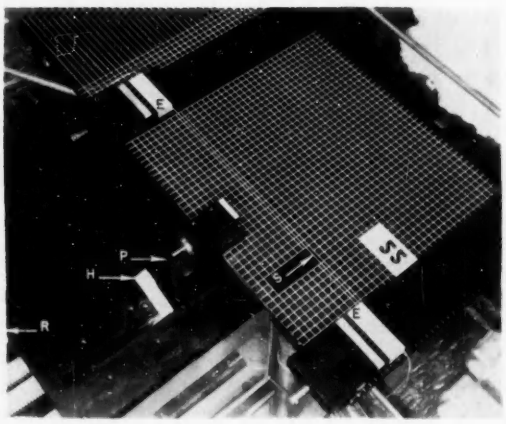

Fig. 2. Detail of yarn impacting apparatus. S yarn specimen, E,E specimen clamps, P projectile, H hammer, R springs.

[1] For high tenacity nylon the magnitude of the longitudinal strain is about 0.3% for a transverse impact velocity of 50 m./sec. and 0.6% for 75 m./sec.

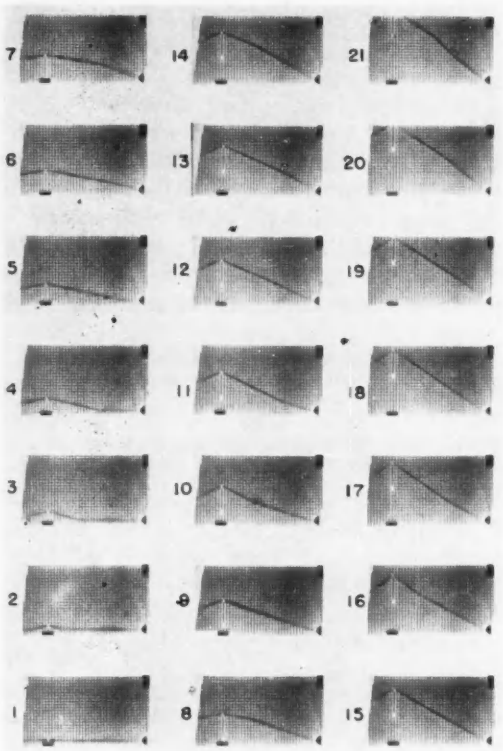

Fig. 3. Film strips showing motion of projectile and configurations of yarn specimen during a transverse impact test. Impact occurred between frames 1 and 2, lower left. Strand by strand breakage began at frame 19, upper right. Camera speed was 6984 frames/sec., but every other frame only was printed in this illustration.

between these wave fronts, the material of the yarn is set in motion toward the point of impact. This inward flowing material forms itself into a tent-shaped wave with the impacting projectile at the vertex. The material forming the tent moves in the direction of the projectile with the velocity of the projectile. The base of the tent propagates outward as a transverse wave with velocity U.

The velocity U is a function of the tension T and strain ϵ in the yarn in the region of the transverse wave front, and of the mass per unit length M of the unstrained yarn. This relationship, derived separately [6, 10], is given by

$$U = \sqrt{\frac{T}{M(1+\epsilon)}} \qquad (1)$$

where U is in Lagrangian coordinates.[2] The transverse wave always propagates more slowly than the longitudinal strain wave.

When the yarn specimen is clamped at two points equidistant from the point of impact, reflections of the longitudinal strain wave will alternately occur at the clamps and at the projectile. At these reflections the local strain increases by small increments. After several of these reflections have occurred and before the rupture strain is attained, the transverse wave front usually arrives at the clamp. As the material forming the tent moves in the direction of the projectile and with the velocity of the projectile, it is apparent that the arrival of the transverse wave at the stationary clamp is equivalent to a new impact giving rise to a new longitudinal strain wave as well as a new transverse wave.

It is appropriate to consider this behavior as a reflection of the transverse wave at the clamp. This reflection is manifested by a marked change in the configuration of the specimen, a sudden increase in

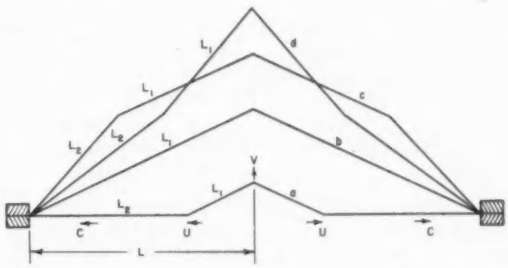

Fig. 4. Typical configuration of yarn specimen after transverse impact. Curve a: Transverse wave propagating outward toward clamps. Curve b: Transverse wave at instant of reflection at clamps. Curve c: Reflected transverse wave propagating inward toward projectile. Curve d: Transverse wave propagating outward again after reflection at projectile.

[2] A Lagrangian system of coordinates is fixed to the specimen, moving and extending with it. For example, in this work the lengths L_1 and L_2 in Figure 4 are transformed to the Lagrangian coordinate lengths $\mathfrak{L}_1$ and $\mathfrak{L}_2$ by the expressions

$$\mathfrak{L}_1 = \frac{L_1 L}{L_1 + L_2}$$

and

$$\mathfrak{L}_2 = \frac{L_2 L}{L_1 + L_2}$$

where L is the distance from the impact point to the clamp in the unstrained specimen. The velocity U is given by

$$U = \frac{d\mathfrak{L}_1}{dt} = \frac{-d\mathfrak{L}_2}{dt}$$

local strain, and a sudden increase in transverse wave velocity. A similar reflection occurs when the transverse wave arrives at the projectile. Again a marked change occurs in the configuration of the specimen, a sudden increase in local strain and a sudden increase in transverse wave velocity occur. These effects are readily discernable in the series of pictures taken with the high speed camera, Figure 3, and in the typical successive configurations a, b, c, and d in Figure 4. In addition to the phenomena just described, interactions will also take place between the longitudinal and the transverse waves. This complex behavior is described in separate papers [6, 10]. It has also been considered theoretically by Craggs [3].

The photographic data, such as that shown in Figure 3, are analyzed as follows. The positions of the transverse wave front, the projectile, and clamp for one side of the yarn specimen are measured from enlargements obtained with a microfilm reader, and configurations of the specimen are drawn on graph paper. The lengths L, L_1, and L_2, as defined in Figure 4, are then measured for the configuration corresponding to each frame of the photographic record, and the average strain $\bar{\epsilon}$ in the specimen computed from the formula

$$\bar{\epsilon} = \frac{L_1 + L_2 - L}{L} \tag{2}$$

From these length measurements the positions of the transverse wave front, given by $\mathfrak{L}_1$ in Lagrangian coordinates are calculated for each frame. The differences between values of $\mathfrak{L}_1$ for successive frames are plotted at each mid-point between these frames, and from the curve obtained the value corresponding to each frame is read off. The velocity U is equal to the product of this quantity by the camera speed in frames per second. The tension in the specimen is then found from the formula [3]

$$T = U^2 M(1 + \bar{\epsilon}) \tag{3}$$

If T is expressed in terms of the more familiar textile unit of grams per denier, and U is in centimeters per second, the equation for tension is

[3] In using this equation, the local strain at the transverse wave front should be used instead of the average strain $\bar{\epsilon}$. This local strain differs at most from the average strain by the magnitudes of the local strain pulses traversing the specimen. At the projectile velocities used in the tests of this paper, these strain pulses are small and the approximation made is warranted.

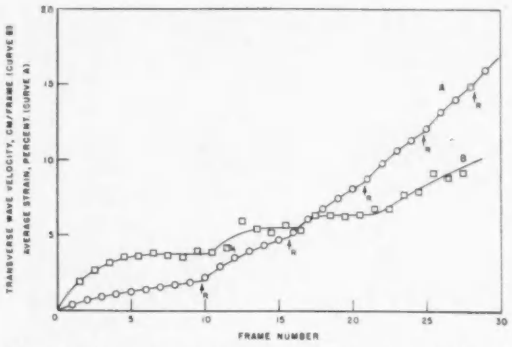

Fig. 5. Average strain and transverse wave velocity as function of time (photographic frame number) for a transversely impacted nylon yarn specimen. Curve A: Average strain versus frame no. Curve B: transverse wave velocity versus frame number. Points R indicate frames in which a reflection of the transverse wave occurred.

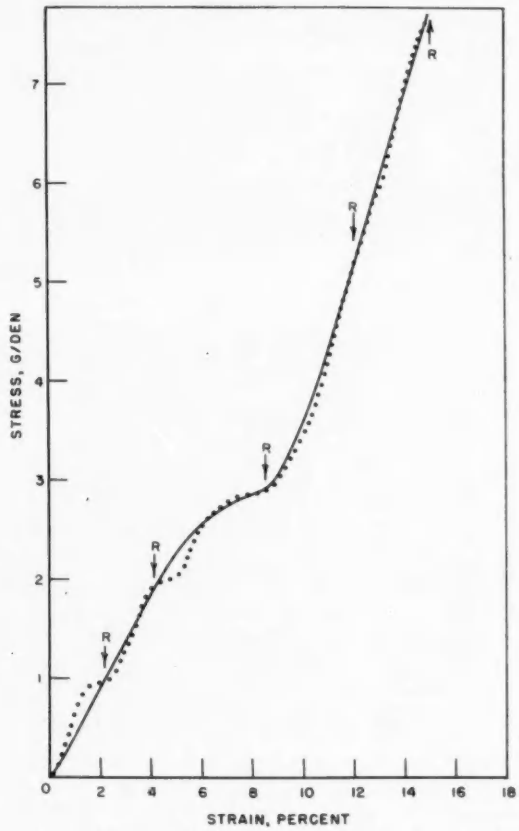

Fig. 6. Stress-strain curve for a transversely impacted nylon yarn specimen. Broken line: Scalloped curve obtained from data shown in Figure 5. Solid line: Smoothed-out stress-strain curve.

$$T = 1.134 \times 10^{-9} U^2 (1 + \bar{\epsilon}) \qquad (4)$$

Typical data from a test with a nylon specimen are shown plotted in Figures 5 and 6. Curve A of Figure 5 is a plot of average strain $\bar{\epsilon}$ versus frame number. The curve is scalloped with abrupt changes in strain occurring at each reflection of the transverse wave (designated by the letter R). The rate of straining increases as the strain increases, causing the stress-strain curve obtained to have a steeper slope at rupture strain than it would have had if the sample had been elongated uniformly at the initial rate.

Elongation at break is estimated from several considerations. Frequently the specimen is seen to break. Often the transverse wave velocity decreases abruptly or the configuration of the specimen becomes irregular, indicating a decrease in tension. Breaking frequently occurs upon reflection of the transverse wave. The time of break can usually be localized to within one frame.

Curve B of Figure 5 is a plot of transverse wave velocity in centimeters per frame versus frame number. This curve is also scalloped, velocity increasing as the tension increases. The character of the scallops indicates how the tension depends upon the local strain.

The dotted line stress-strain curve in Figure 6 is obtained by plotting data taken from Figure 5. The scallops are due principally to use of the average strain $\bar{\epsilon}$ in the plotting and the calculations, rather than the local strain at the transverse wave front. The average strain just before reflection of the transverse wave (indicated by the letter R) most closely approximates this local strain. The smoothed stress-strain curve shown as a solid line is drawn through these points.

As an indication of the reproducibility of this method for obtaining stress-strain curves, data from a number of tests on nylon yarn specimens are presented in Table I. It is evident from these data that if duplicate tests are made with transverse impact velocity and specimen length kept constant, the values obtained for breaking tenacity, breaking strain, and initial modulus are in good agreement. Moreover these properties are not affected greatly by the range of impact velocities and specimen lengths used in these tests.

TABLE I. Transverse Impact Data for High Tenacity Nylon

Test	Impact velocity, m./sec.	Specimen length, cm.	Rate of straining, %/sec.	Time to break, sec.	Initial tensile modulus, g./den.	Breaking strain, %	Breaking tenacity, g./den.
6T	45.3	60	1500–7000	3.73×10^{-3}	50	14.8	7.50
7T	43.0	60	1000–5000	3.92	65	14.4	7.10
42T LH	44.9	40	2000–9500	2.62	50	15.0	7.60
RH	44.9	40	2000–8500	2.62	60	14.7	6.10
74T LH	42.2	40	2000–8000	2.59	50	13.2	8.60
RH	42.2	40	2000–6500	2.59	50	13.1	7.10
75T LH	42.5	40	2000–6000	2.74	50	15.5	8.70
RH	42.5	40	2000–8500	2.68	55	14.5	7.85
18T	65.7	60	2500–9500	2.70	65	15.0	7.10
19T	66.4	60	2500–9000	2.67	60	15.3	6.80
76T LH	62.5	40	4500–12,500	1.74	60	14.8	8.20
RH	62.5	40	4000–12,500	1.74	65	14.8	9.20
77T LH	64.2	40	4000–14,500	1.83	60	15.6	7.40
RH	64.2	40	4000–14,000	1.83	65	15.7	6.75

Nylon tested was du Pont, type 300, 5 ply, 210 den. per ply, 3 Z twist, 1085 den. total, obtained from U.S. Army Q.M. Specimens were impacted transversely midway between clamps. In tests 42T and 74T to 77T, the lengths were sufficiently short that the entire specimen could be photographed and separate analyses made for the segments on each side of the impacting projectile.

In Table I, tests 6T and 7T, in which the specimen half length L is 30 cm. have an average breaking time of 3.8×10^{-3} sec. and an average breaking strain of 14.6%. The corresponding average rate of straining is thus 4000%/sec., roughly. Similarly for tests 42T, 74T, and 75T, in which L is 20 cm., the average rate of straining is 5500%/sec. Of the tests conducted at 65 m./sec., 18T and 19T, for which L is 30 cm., have an average rate of straining of 5500%/sec., and 76T and 77T, with L 20 cm., have an average rate of straining of 8500%/sec. Curves of average data for the four tests just described are plotted in Figure 7. These four curves do not differ greatly so the curve of average data for all the tests listed in Table I may be considered representative. This curve is plotted in Figure 8, and the rate of straining assigned is 5000%/sec.

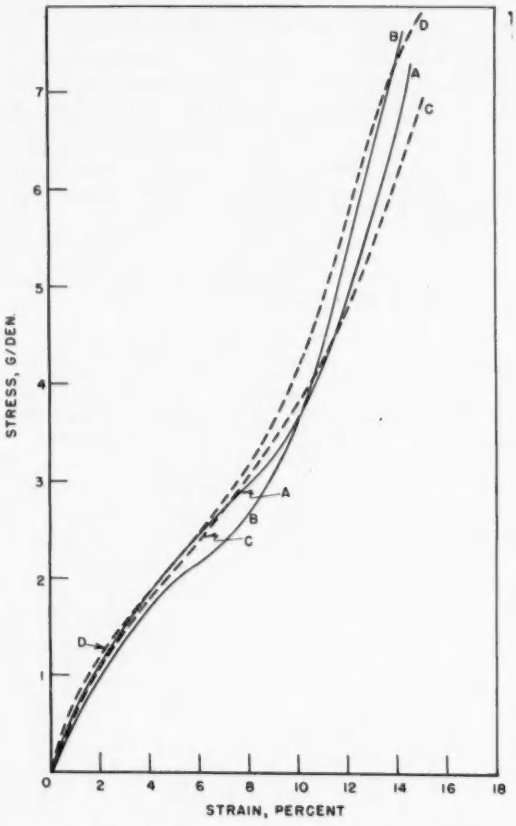

Fig. 7. Stress-strain curves for high tenacity nylon specimens impacted transversely. A. Impact speed 45 m./sec., half-length 30 cm., rate of straining 4000%/sec. B. Impact speed 45 m./sec., half-length 20 cm., rate of straining 5500%/sec. C. Impact speed 65 m./sec., half-length 30 cm., rate of straining 5500%/sec. D. Impact speed 65 m./sec., half-length 20 cm., rate of straining 8500%/sec.

The stress-strain curves for nylon at low rates of straining, plotted in Figure 8 were obtained with an Instron tensile tester.[4] These curves are average data from five tests each on specimens 10 in. long. The specimens were conditioned and tested at a temperature of 72° F. and relative humidity of 50%. (The temperature and humidity in the room where the transverse impact tests were made were not controlled).

Similar data for Fortisan and Fiberglas are presented in Figures 9 and 10 and in Tables II and III. Table IV summarizes the average data characterizing the curves plotted in Figures 8 through 10. In comparing the data for nylon, Fortisan, and Fiberglas, it is seen that in each case increasing the rate of straining tends to make the slope of the stress-

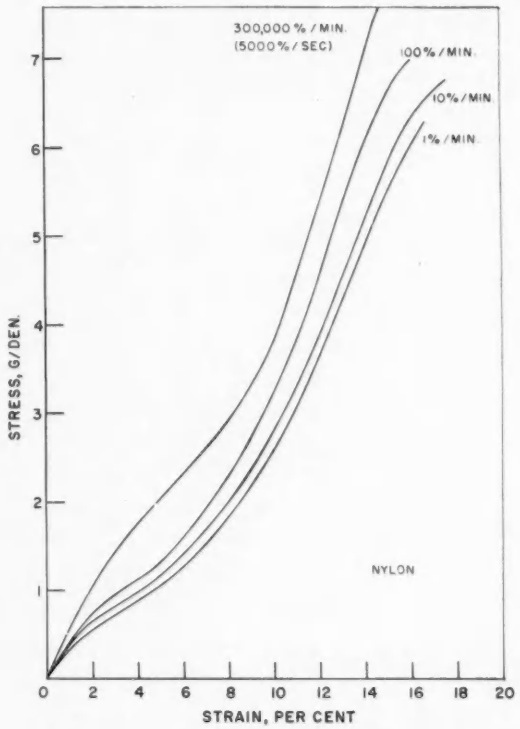

Fig. 8. Stress-strain curves for high tenacity nylon at various rates of straining.

[4] Manufactured by the Instron Engineering Corporation, Quincy, Mass.

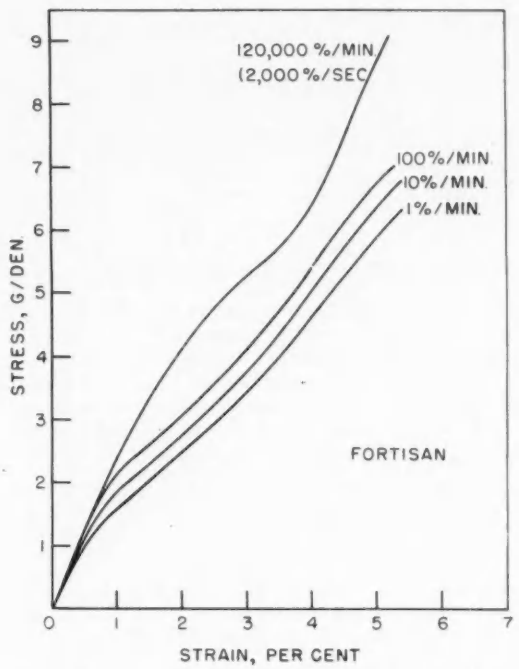

Fig. 9. Stress-strain curves for Fortisan at various rates of straining.

strain curve steeper at the origin; i.e., increases the initial tensile modulus. In addition the initial linearity of the stress-strain curve persists up to increasingly large values of the stress. This type of behavior has previously been observed by Meredith for textile yarns [7], by the authors for hair [8], and by Campbell for mild steel [1]. It is similar to the type of behavior observed when the stress-strain curve is obtained at standard rates of straining, but at low temperatures. Typical curves for specimens measured under these conditions have been published by Kaswell [4] and Coplon [2].

The stress-strain curves for Fiberglas, Figure 10, become increasingly linear in the rate of straining range 1%/min. to 100%/min. However, the nonlinearity of the 1%/min. curve may be attributed in part to filament slippage. The 1000%/sec. curve is slightly concave upward. This latter effect may be attributed to the increase in rate of straining which occurs in this method at increasing stress.

Acknowledgment

The support of this work by the Quartermaster Research and Development Command, U.S. Army and permission to publish are gratefully acknowledged.

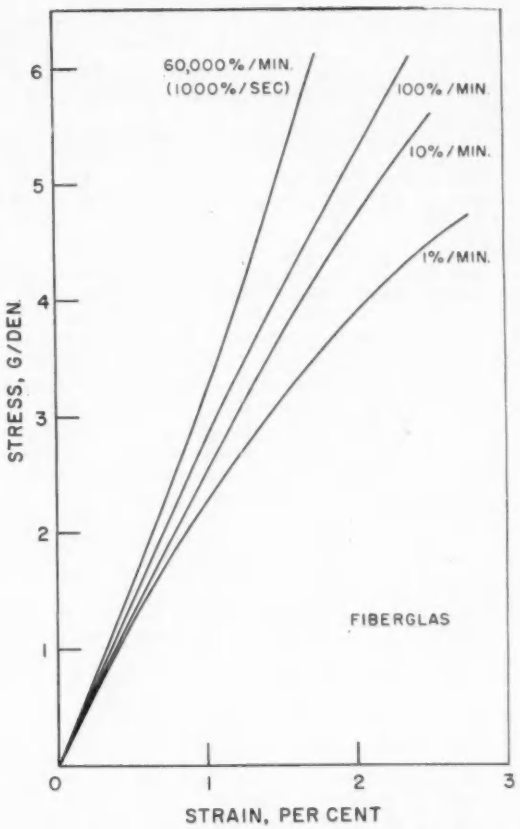

Fig. 10. Stress-strain curves for Fiberglas 150-1/0 at various rates of straining.

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TABLE II. Transverse Impact Data for Fortisan

Test	Impact velocity, m./sec.	Specimen length, cm.	Rate of straining, %/sec.	Time to break, sec.	Initial tensile modulus, g./den.	Breaking strain, %	Breaking tenacity, g./den.
8T	46.2	60	1000–4000	1.70×10^{-3}	260	4.5	8.70
81T	40.6	60	1000–3500	2.53	250	5.9	9.20
82T	41.3	60	1000–3500	2.50	260	5.7	9.70
83T	41.2	60	1000–3500	2.47	250	5.3	10.10
84T	41.3	60	1000–3000	2.35	260	4.7	7.80

Fortisan tested was a high tenacity deacetylated cellulose acetate yarn, 3 ply, 270 den./ply, 2.5 Z twist, 787 den. total, obtained from the Celanese Corporation of America.

TABLE III. Transverse Impact Data for Fiberglas

Test	Impact velocity, m./sec.	Specimen length, cm.	Rate of straining, %/sec.	Time to break, sec.	Initial tensile modulus, g./den.	Breaking strain, %	Breaking tenacity, g./den.
24T	41.9	60	900–1700	1.41×10^{-3}	320	1.76	5.65
91T	41.0	60	800–2000	1.40	320	1.70	6.65
92T	43.1	60	900–2100	1.48	320	1.75	6.75
93T	39.9	60	1000–2000	1.50	330	1.70	5.15
94T	40.0	60	700–2000	1.51	330	1.81	6.40

Sample tested was Fiberglas 150–1/0, 1 Z (323 den.) obtained from the Owens-Corning-Fiberglas Corp.

TABLE IV. Tenacities, Elongations, and Initial Tensile Moduli for Nylon, Fortisan, and Fiberglas

Material	Rate of straining, %/min.	Initial tensile modulus, g./den.	Elongation at break, %	Tenacity at break, g./den.
High tenacity nylon	1	36	16.7	6.28
	10	41	17.6	6.76
	100	45	16.1	6.97
	300,000 (5000%/sec)	57	14.7	7.57
Fortisan	1	168	5.4	6.33
	10	199	5.4	6.80
	100	251	5.3	7.04
	120,000 (2000%/sec.)	256	5.2	9.10
Fiberglas	1	249	2.8	4.73
	10	260	2.5	5.58
	100	279	2.4	6.07
	60,000 (1000%/sec.)	324	1.8	6.12

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Water Transport Mechanisms in Textile Materials[1]

Part I: The Role of Yarn Roughness in Capillary-Type Penetration

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Abstract

The movement of liquid water in fiber assemblies such as yarns and fabrics is examined in terms of a theory of water transport based on a capillary penetration mechanism. Yarn construction features, such as twist, diameter, crimp, and fiber denier, are shown to be related to the rate of water transport in such fiber assemblies. From measurements of yarn and fiber water contact angles, it is shown that water transport in yarns is only slightly influenced by the wetting properties of the individual fiber materials and depends mainly on the wetting behavior of the whole yarn. Increase in yarn roughness due to random arrangement of its fibers gives rise to a decrease in the rate of water transport, and this is seen to depend on two factors directly related to water transfer by a capillary process. (1) The effective advancing contact angle of water on the yarn is increased as yarn roughness is increased. (2) The continuity of capillaries formed by the fibers of the yarn is seen to decrease as fiber arrangement becomes more random. The measurement of water transport rates in yarns is thus seen to be a sensitive measure of the properties of fiber arrangement and yarn roughness in textile assemblies. The present studies on cotton, nylon, Dacron, wool, and wool blended yarns thus indicate that an appropriate choice in fiber crimp, fiber denier, yarn size, and blend uniformity are all important in obtaining blended fabrics of desired properties.

Introduction

The processes whereby moisture may be transported through textile materials may be conveniently divided into those involving the diffusion of water vapor and those involving the transport of liquid water. The latter has been a subject of study for fabrics of many kinds but usually in connection with the water repellency of such materials. The advent of synthetics and blends of these with wool and the observation that synthetic-rich blends are usually easily wet with water has led to a shift in emphasis in the studies of the relation of water to fabric properties. Accordingly, in general studies on blended fabrics, attempts have been made to evaluate their wicking behavior, so named because of the experimental practice of following the rise of water in wicks of fabric materials [8]. The present discussion is concerned with the reasons for differences in wicking in various fabric blends. In this work, the movement of water in fiber assemblies has been analyzed in terms of the fiber properties and yarn structure.

[1] This work constitutes a part of the Army Quartermaster program of research on warmth and comfort of military fabrics, performed under contract QM 564.

The mechanisms which may operate to move fluids through porous materials are numerous [2], but the viscous flow of water through the capillaries of a porous medium accounts for the major portion of the water transfer [9]. Application of the classical work of Washburn [22] on the hydrodynamics of capillary flow has met with considerable success in its application to water penetration in paper materials [13, 17]. Similar analyses have been successful in studies on soil [5] and leather [21].

The treatment of fiber assemblies as bundles of capillaries has found suitable confirmation in other types of water transfer work [16, 18], but the relation of yarn geometry and surface roughness of fibers and yarns to water movement in textile assemblies is less well understood. These factors are considered in some detail in this presentation.[2]

Capillary Water Transport in Yarns

(*a*) *Theory*

From considerations of the laws of hydrodynamic flow through the capillaries formed by fibers in tex-

[2] The effects of yarn geometry and surface roughness on the over-all water transport properties of blended fabrics [15] and on the thermal conductivity of these fabrics [7] are given in separate descriptions of these studies.

tile assemblies, it can be shown that

$$s^2 = \frac{\gamma \cos \theta'_A}{2\eta} r_e t = k_s t$$

(Equation 15, Appendix I)

(The derivation of this equation is given in Appendix I.) In this expression s is the horizontal distance traveled by a liquid of surface tension γ and viscosity η through capillaries of effective radius r_e in time t. The capillaries are wet at an apparent advancing contact angle θ'_A which differs from the advancing contact angle θ_A of the fiber material in proportion to the roughness of the yarn containing these capillaries. The rate of water transport k_s is thus a constant for the penetration of a given liquid into a definite assembly of fibers.

(b) Experimental

Examination of the vertical wicking behavior of several experimental blended fabrics [8] indicated that the yarns were responsible for the main portion of the wicking action of these fabrics. The transport of water in yarns was studied microscopically using a mechanical stage, an objective magnification of 5×, and a filar eyepiece of 12.5× magnification. Yarns were mounted on the microscope stage parallel to a stainless steel rule. A drop of 0.05% solution of a blue dye (Ink Blue BJTBNA) was placed on one end of the yarn and the position of the head of liquid followed as a function of time. Dye in this concentration had no measurable effect on the rate of water transport. Measurements of the yarn diameter before and after being wet were obtained with the filar eyepiece. It was observed that the average wet diameter was most useful for calculation of the mean capillary radius. A means for obtaining the mean capillary radius from yarn geometry is given by Equation 17 of Appendix II.

In Figure 1, in which the square of the distance of water travel is plotted against time, are water transport curves for several yarns examined by this technique. The linearity of the water transport curves gives a good indication that Equation 15 applies to water flow in widely different types of yarns. Accordingly, slopes of the curves were used to obtain water transport rate constants for yarn fiber assemblies.

For some of the work, yarnlike structures were made in the laboratory by twisting filaments together in a twist counter, and these are called "simulated" yarns in the results which follow, to differentiate them from those spun in the mill by conventional manufacturing operations.

The Influence of Yarn Geometry on Wicking

The flow of water in several simulated yarns made from nylon filament was examined by the microscopic technique, and results of these experiments are summarized in Table I. By altering the

TABLE I. Water Transport in Simulated Nylon Yarns

Yarn twist (t.p.i.)	No. of fibers	Fiber size (den.)	Water transport constant, k_s (cm.²/sec. ×10²)	Mean capillary radius, r* (μ)	Normalized transport constant† (cm.²/sec. ×10²)
2	100	3	4.4	17.7	2.8
3	60	3	2.6	9.8	3.0
3	60	15	3.6	17.0	2.8
6	30	3	2.2	9.0	2.9
12	30	3	2.6	11.1	3.1

* Calculated directly from yarn size, number of fibers, and fiber size, using Equation 17.

† Corrected for twist tortuosity, using Equation 18, and normalized to a mean capillary radius of 10 μ, using Equation 16, Appendix II. For the latter correction to apply quantitatively, changes in the type of fiber arrangement in the yarn must be negligible.

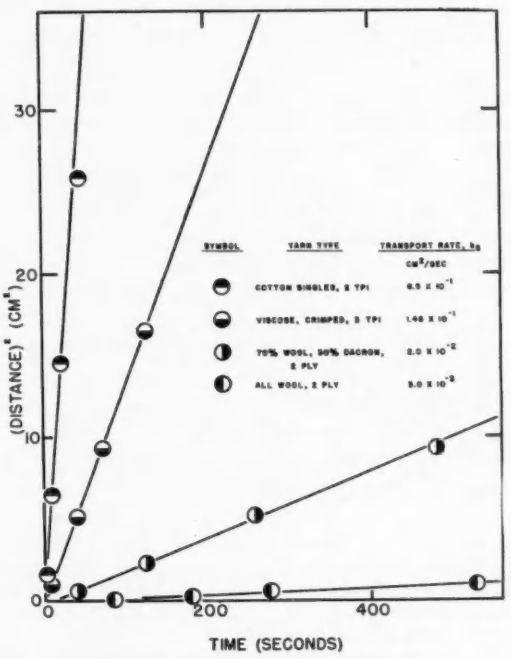


Fig. 1. Yarn-water transport curves.

yarn twist, fiber denier, and number of fibers in the yarn, it was possible to test the water transport equation for yarns having several different capillary sizes. The results of Table I show that the water transport rates corrected for differences in capillary radius are indeed constant for yarns made from the same fiber material. This evidence likewise supports the form of the capillary water theory given by Equation 15.

Similar studies made on yarns taken from several serge fabrics of differing fiber composition and water transport rates for these as a function of yarn twist are given in Figure 2. Over the twist range of 4 to 12 t.p.i. the change of water transport rate followed the capillary transport laws fairly closely, high twist yarns exhibiting low rates. At lower twists the decrease in transport rate for all three yarn types studied was apparently due to a substantial reduction in the number and continuity of the interfiber capillaries. Reasons for the differences in absolute value of the transport rates for yarns made from different fiber materials are considered along with yarn–water contact angles in the next section.

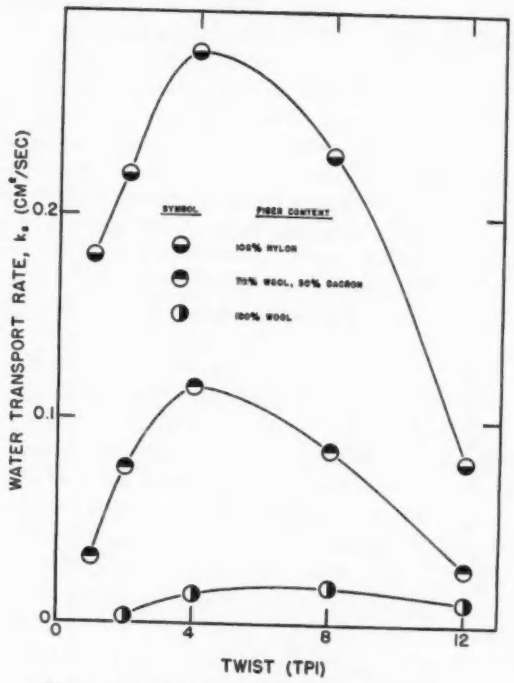


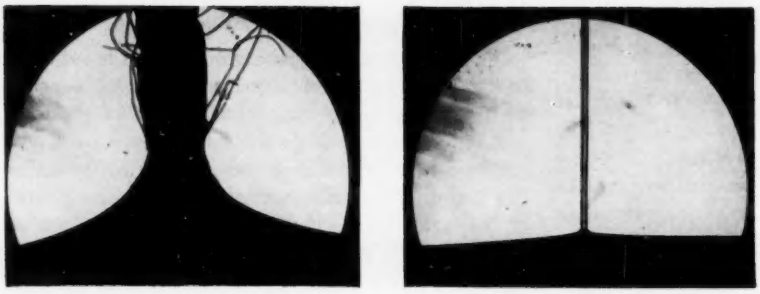
Fig. 2. Effect of yarn twist on rate of wicking, singles yarns from serge fabrics.

Contact Angles of Water with Fibers and Yarns

The ease of wetting of a solid, which is reflected in the contact angle measured in the liquid, depends to a large extent on the actual nature of the solid surface. For example a sorbed film on a solid surface may entirely determine its wetting behavior [12], and in a similar manner, physical roughness of the solid surface may exert a large influence on the ease with which it is wet [20]. For textile materials in the form of yarns or individual fibers, both these factors may operate to determine their wetting properties, and it is for this reason that the water transport equation (15) contains an apparent advancing contact angle θ'_A instead of the value θ_A used for a clean smooth surface. For yarns in particular then, θ'_A is an empirical measure of the surface roughness of the yarn as determined by the arrangement of the individual fibers in this structure.

In order to appraise the effects of surface roughness on actual water transport rates in fiber assemblies, contact angles of water on yarns and fibers were measured, using the vertical rod method of Bartell *et al.* [3]. Advancing and receding contact angles were measured from the image projection of the solid–water interface, and some of these are shown in the photographs of Figures 3. The angle between the edge of the solid surface and a line drawn tangent to the solid–water interface at the intersection of the solid–air–water phases was used as the apparent contact angle. The effects of the yarn surface are clearly seen in comparing this angle for the nylon yarn in Figure 3*a* with a nylon fiber in Figure 3*b*, the yarn giving a much lower contact angle than the single fiber.

In general, 10 to 20 measurements of contact angles were made on each yarn or fiber studied and averages of these values are used in presentation of the data. In order to ensure that contact angles were measured on solid surfaces of the same state of cleanliness, two precautions were observed. The fibers and yarns were laundered and rinsed in distilled water, then conditioned to approximately 65% relative humidity at room temperature. This procedure ensured that the fiber and yarn surfaces were in a state of surface cleanliness comparable to what they would have in actual use and that any effects on the contact angles due to water sorbed on the surface of the fibers would be similar to those encountered in the use of these materials under practical atmospheric conditions.



a b

Fig. 3. Apparent water contact angles on textile materials. *a*, Nylon yarn; *b*, nylon fiber.

In Table II are advancing and receding angles obtained for a number of fibers and yarns taken from the same source. With the exception of the polyethylene filaments, fibers and yarns were taken from serge fabrics of conventional design, using staple fibers. Synthetic fibers in these materials were 3 den. and wool 58–60's U.S. grade. For the polyethylene, nylon, Dacron, and wool fibers studied, the advancing contact angles were about the same and sufficiently high to indicate that these were nonwettable surfaces. The receding angles, on the other hand, were lower, and as suggested by Baxter and Cassie [6], probably resulted from the formation of a film of water on the fiber surfaces.

Extraction of the wool fiber with organic solvents lowered even the advancing contact angle in agreement with the findings of Preston *et al* [19], and probably resulted from the formation of a stable water film on the cleaned protein surface.

TABLE II. Apparent Contact Angles of Water on Fibers and Yarns

Material	Form	Advancing angle (deg.)	Receding angle (deg.)
Polyethylene	Fiber	86	49
	Yarn	25	16
Nylon	Fiber	83	60
	Yarn	55	33
Dacron	Fiber	79	74
	Yarn	49	20
Wool	Fiber	85	34
	Yarn	108	21
Wool*	Fiber, 1 extraction	87	38
	Fiber, 2 extractions	77	38
	Fiber, 3 extractions	65	37

* These fibers were extracted in warm ether, alcohol, and water.

A comparison of the yarn and fiber advancing contact angles in Table II shows that the yarns made of synthetic fibers give angles lower than those of the individual fibers, while the wool yarns exhibit contact angles higher than those for the single wool fibers. This type of behavior for wool yarns has been studied in some detail [6] and forms the basis for a water repellency mechanism defined in terms of fiber spacing and fabric structure [10]. Although the ease of wetting of yarns from synthetic fibers is a matter of common experience, it is clear from Table II that they differ from wool yarns in the yarn–water contact angle, rather than in the wetting behavior of the fiber materials themselves. Therefore, it is the differences in yarn surface roughness which give rise to differences in wicking of yarns and in fabrics made from the yarns. Wool fibers form rough yarns of high apparent contact angle because of the natural crimp and more random distribution of fibers in the yarns, whereas the yarns of synthetic fibers are compact, well-aligned, and hence smooth in terms of contact angle. This type of behavior is in agreement with evidence from the wicking and structural properties of different blended fabrics discussed in a previous study [8].

Further information on the relation of yarn and fabric structure to wetting behavior can be obtained from a comparison of the apparent advancing contact angles with actual water transport rates for yarns and fabrics. Data of this type for yarns from several serge and underwear fabrics are summarized in Table III. The water transport rates for the fabrics were obtained by a method similar to that used for the yarns, and this is described in a separate publication [15].

Although for most of the yarns studied the correlation between water transport rates and cosine of the contact angle is fairly good, above an angle of

approximately 65°, the water transport figures for yarns and fabrics are several orders smaller than would be predicted from the magnitude of $\cos \theta'_A$. If the low rates were due only to contact angle effects, we should expect this behavior to occur only at angles near 90°. The explanation lies in taking into account the decrease in continuity of the interfiber capillaries, which accompanies an increase in yarn roughness, and which leads to large changes in the effective capillary radius of the assembly. In yarns with fibers arranged in a relatively disorderly manner, capillary continuity is poor, and this is reflected by abrupt changes in the water transport rate over the length of such a yarn. Indeed in wicking studies on yarns from wool blend fabrics in which blending was not particularly even, there was sometimes sufficient discontinuity to cause wicking to cease at some point along the length of the yarn.

Actually, cessation of wicking in yarns can occur for another reason which is not reflected in the apparent contact angle. Instead it is related to the value of the effective capillary radius r_e, and can be seen in calculations of the mean capillary radius $\bar{r}$. In high twist yarns of swelling fibers such as are used in smooth finished rayon fabrics, wicking may cease as the capillary spaces begin to close up due to fiber swelling. This explanation is strengthened by the fact that the calculated values of the mean capillary radius approach zero. The retardation of the flow of water along such a yarn is greater than that which would be predicted by Equation 15 as drag on the walls of the capillaries becomes an important resistive force to capillary action [14]. A few instances of wicking curves of this type were observed.

TABLE III. Apparent Advancing Contact Angles θ'_A for Yarns and Water Transport Rates k_z for Yarns and Fabrics

Sample no.	Fiber material	Yarn angle θ'_A (deg.)	Cosine angle $\cos \theta'_A$	Yarn transport rate k_z (cm.²/sec.)	Fabric transport rate k_z (cm.²/sec.)
Serges					
48	Cotton	18	0.95	0.45	0.16
N2	Nylon	29	0.87	0.23	0.11
A	Wool	108	Negative	0.001	0.005
Underwear					
62	Nylon	50	0.64	0.15	0.16
65	Nylon, w.r.*	128	Negative	<0.001	<0.001
68	Cotton	33	0.84	0.21	0.20
70	Wool, s.r.†	43	0.73	0.033	0.029
86	Wool	68	0.37	<0.001	<0.001

* Water-repellent.
† Shrink-resistant.

Conclusions and Discussion

Experimental examination of the rates of transport of liquid water along a wide variety of yarns supports the view that water travel occurs essentially by capillary action. Yarn construction features, such as size, number of fibers, fiber size, and twist, all affect the rate of water transport insofar as they control the size of the interfiber capillaries, large capillaries in general producing higher wicking rates. Contact angle measurements on yarns and fibers from the yarns have shown that water motion in yarns is directly related to the apparent advancing contact angle of water on the yarn and only indirectly to the surface properties of the fiber material.

Yarns differ widely in surface roughness. Fuzzy yarns containing randomly arranged fibers are usually nonwetting because of high water contact angles. In addition, they contain discontinuous capillaries ill-suited for capillary action. Natural or artificial fiber crimp and evenness of blending in blended yarns are important factors in determining the extent of surface roughness and capillary continuity.

Work on the thermal properties of textile assemblies [7] has clearly shown that their insulating ability also depends on the randomness of the fiber arrangement in the fabrics. It seems, then, that it should be possible to control or alter the wicking and thermal properties of blended yarns and fabrics by changes in yarn construction and in methods of manufacture which directly affect yarn evenness. The results of pilot scale trials in this direction will be described in a subsequent publication.

APPENDIX I

Theoretical Development of the Capillary Water Transport Equation

The fundamental formulae of capillary penetration may be deduced from the existence of free surface energy at any interface between phases of different composition [1]. This free surface energy arises from the inward attraction of the underlying molecules for those in the surface, and since a surface possessing free energy contracts when free to

do so, the free surface energy is also called surface tension.

Dupré's equation

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad (1)$$

relates the work of adhesion W_{SL} required to separate unit area of the solid and liquid contact to the surface tensions γ_{SA} and γ_{SL} of the solid against air and liquid and the surface tension of the liquid γ_{LA}. Liquids usually rest on solids at a definite angle θ (measured in the liquid). The relation between surface tensions and contact angle may be deduced by treating the surface tensions as mathematical forces pulling parallel to each surface, and resolving parallel to the solid surface. The resulting expression is

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos\theta \quad (2)$$

Combining (1) and (2) to eliminate the solid surface tensions

$$W_{SL} = \gamma_{LA} (1 + \cos\theta) \quad (3)$$

which is known as Young's equation.

The surface area of a liquid-air interface is unique, and may always be identified with its plane geometrical area, but the surface of a solid-liquid interface depends very much on the condition of the solid surface. Wenzel [23] proposed that if a solid surface is roughened so that unit plane geometrical area has an actual surface area R times that of the smooth surface, the energy gained in forming the solid-liquid interface will be $R(\gamma_{SA} - \gamma_{SL})$ and the apparent contact angle θ' of the roughened surface will be given by

$$\cos\theta' = \frac{R(\gamma_{SA} - \gamma_{SL})}{\gamma_{LA}} = R\cos\theta \quad (4)$$

Alternatively Bartell and Shepherd [4] have proposed that where the microscopic cavities of the rough surface make an angle ϕ with the general direction of the solid surface, the apparent contact angle

$$\theta'_A = \theta + \phi \quad (5)$$

for liquids advancing over a surface or

$$\theta'_R = \theta - \phi \quad (6)$$

for liquids receding over a surface. It is also permissible to include in θ'_A effects due to sorbed material on the fiber surface. For the experimental work presented in this paper, θ'_A is used to represent both surface film and surface roughness effects of the solid material.

When a liquid enters a capillary of small radius, a curved meniscus will be set up unless the contact angle is exactly 90°. The radius of curvature of the meniscus is $r/\cos\theta$, and the pressure causing penetration into the capillary [5] is

$$p = \frac{2\gamma\cos\theta}{r} \quad (7)$$

where $\gamma = \gamma_{LA}$. The contact angle varies, however, with the tendency of the liquid to move along the surface, being a maximum when the liquid is advancing over a dry surface. Then for a meniscus moving slowly into a capillary, the driving pressure is

$$p_i = \frac{2\gamma\cos\theta_A}{r} \quad (8)$$

or for rough capillary materials (Equations 4 or 5)

$$p_i = \frac{2\gamma\cos\theta'_A}{r} \quad (9)$$

The viscosity of liquids exhibiting laminar flow through capillaries is related to the capillary size and liquid properties by Poiseuille's equation

$$\eta = \frac{\pi p r^4}{8vl} \quad (10)$$

when p is the driving force on a liquid of viscosity η, passing through a capillary of radius r and length l, and with a volume v flowing through the cross section in unit time. The corresponding expression [5] in terms of the velocity of the liquid u is

$$u = \frac{r^2 p}{8\eta l} \quad (11)$$

For a liquid penetrating a horizontal capillary, no gravitational force is involved. In addition, because the acceleration is small, we may neglect inertial forces and simply equate the surface and viscous forces at the surface [11]. Accordingly, using Equation 9 in Equation 11

$$u = \frac{\gamma\cos\theta'_A r}{4\eta l} \quad (12)$$

If capillary penetration occurs to distance s in time t, then $u = ds/dt$ and $l = s$. Hence

$$sds = \frac{\gamma\cos\theta'_A r dt}{4\eta} \quad (13)$$

Integrating

$$s^2 = \frac{\gamma\cos\theta'_A rt}{2\eta} \quad (14)$$

If we consider fibers in textile assemblies form capillaries of effective radius r_e, then the horizontal

water transport rate becomes

$$s^2 = \frac{\gamma \cos \theta'_A r_e t}{2\eta} = k_s t \qquad (15)$$

where k_s is the capillary water transport constant for the material.

APPENDIX II

Auxiliary Equations

It is useful to describe the effective capillary radius r_e in terms of the mean capillary radius $\bar{r}$, formed by fibers in yarns by means of the expression

$$r_e = \bar{r} f(y) \qquad (16)$$

in which $f(y)$ is a continuity and distribution function for capillaries in a real yarn. As has been shown by Palmer [16], $f(y)$ would equal $1/k^2$ where k is a tortuosity factor for porous media having a very uniform distribution of capillary sizes. However, the function $f(y)$ cannot have any simple form for a system as heterogeneous as a fiber assembly, and no attempt is made in the present discussion to ascertain what form it would take. Instead, if we assume the function is roughly constant for assemblies of similar construction, then it suffices to evaluate the mean capillary radius $\bar{r}$ for the comparison of real fiber assemblies. For circular yarns of diameter D, containing n circular fibers of diameter d,

$$\bar{r} = \tfrac{1}{2}(D^2/n - d^2)^{\frac{1}{2}} \qquad (17)$$

The twist in yarns influences the length of the interfiber capillaries as a result of the helical path of the fibers in the yarn. If k_s° is the horizontal water transport constant corrected for this effect, then

$$k_s^\circ = k_s(1 + 0.87\, DT_w)^2 \qquad (18)$$

in which T_w is the twist of the yarn. The equation assumes that all capillaries are continuous along the length of the yarn and that the helix formed by any one capillary does not change in diameter over this distance. Examination of rate data for a large number of yarns has shown that this model is a sufficiently good approximation to the structure of a real yarn to provide a satisfactory correction for yarn twist in water transport data.

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The Application of Crease-Resistant Finishes to Cotton

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Introduction

The commercial production of crease-resistant cellulosic fabrics by the application of amino-resins has now been practiced for at least 25 years, and the principal requirements of such processes are well understood. It was appreciated at an early date that in order to obtain successful results, the resin should reside within the cellulose fibers. Surface resin should be kept to a minimum, since it produces undesirable effects on the handle and wearing properties of the treated fabric. For this reason, the resin precondensate employed should be of low molecular complexity, so as to enable the molecules to penetrate the amorphous regions of the cellulose.

Resin precondensates of the same type will impart crease-resistant properties to both cotton and viscose rayon, but the secondary effects on fabric properties associated with the resin treatment of these two fibers differ in certain respects. The dry tensile strength of treated viscose rayon is usually higher than that of the untreated fabric, while the wet tensile strength shows considerable improvement. In the case of cotton, the wet and dry tensile strength may both be considerably reduced by resin treatment. The tear strength of both cotton and viscose rayon is lowered by resin application, but this effect is commercially significant on cotton only, the tear strength of rayon being generally higher initially. Laboratory assessments of wearability, based on various abrasion tests, show a considerable drop with respect to cotton, but rayon is relatively unaffected, provided that the resin has been correctly applied. The interpretation of such results is difficult, and it has been suggested that accelerated wear tests frequently bear no relation to the results of actual wearer trials [11]. Nevertheless, the difference in mechanical behavior between treated cotton and rayon is clearly evident. This fundamental difference appears to be closely connected with the physical and chemical differences between natural and regenerated cellulose, although the mechanism involved has not been adequately explained. Whatever this mechanism may be, it has been established that removal of the resin finish by suitable stripping treatments will frequently restore the original properties of the fabric.

The tensile and tear strength of crease-resistant viscose rayon are both adequate for commercial purposes, but this is not necessarily so in the case of treated cotton, and numerous suggestions have been put forward in an effort to improve the results obtained. One of the earliest of such proposals was mercerization of the fabric prior to resin treatment [2, 18], and this procedure is well established commercially. Other suggested expedients include the incorporation of various thermoplastic additives in the padding solution [3, 4, 8], while the use of cationic softeners has also been proposed [1, 15].

The work described below comprises an examination of some of these suggestions and an investigation of the influence of a number of other factors on the strength of the treated cotton. These include the type of resin precondensate used, its molecular size, and the degree of cure obtained. Further experiments have been carried out to examine the effect on fabric strength of washing off after resin treatment. A preliminary assessment of the influence of the construction of a fabric on its strength after crease-resisting has also been made. A discussion of the results obtained is followed by an attempt to explain the differences in behavior between natural and regenerated cellulose in terms of the known differences in structure between the two fibers.

Experimental Work

A description is given below of the procedure adopted for treating fabric samples with resin precondensates in the laboratory. The operating technique has been kept constant as far as possible and has only been varied for the purpose of specific experiments, such as those involving different curing times and temperatures. The methods of testing the treated fabrics are also outlined.

(*a*) *Application of the Resin Precondensate to the Fabric*

The resin solution was prepared by diluting the concentrated resin if liquid, or dissolving if solid, by addition of soft water (steam condensate) to nearly the volume required, adding the accelerator as an aqueous solution of suitable concentration and diluting with soft water to the required volume.

The fabric employed in most of the work was an 80 × 80 plain weave cotton of about 3½ oz. to the square yard. In some experiments on mercerization, a 55 × 45 plain weave cotton of heavier weight was used, while some comparative experiments on viscose rayon staple were performed with Utility 1009 fabric. A number of other fabrics were used in experiments on cloth construction, and these will be described later.

Pieces of the appropriate material 11 in. wide were cut in the weft direction and padded weft-ways after immersion in the resin solution. The mangle employed was an Acme Domestic Wringer, and the pressure was adjusted so that the pickup was 100%. This was checked by weighing the fabric before and after impregnation and mangling. The treated material was suspended from glass rods and allowed to dry in the air at laboratory temperature, the pieces being reversed at frequent intervals to prevent drainage of resin down to one end of the sample. When apparently dry to the touch, after a time dependent on the prevailing temperature and relative humidity, the samples were finally dried in an oven for 15 min. at 85° C. and immediately transferred to the curing oven. The normal curing time was 10 min. at 140° C., which experience has shown to give a degree of cure similar to that obtained commercially. The ovens used were electrically heated, thermostatically controlled and equipped with fans to improve air circulation, while only one sample was placed in the ovens at one time.

(*b*) *Washing Off*

Where this operation has been carried out, the procedure has been to immerse the sample in 0.2% soap solution at 40° C. for about 1 min., rinse in two separate lots of soft water at 40° C., and finally air-dry.

(*c*) *Testing Procedures*

(i) *Degree of cure.* The nitrogen content of a portion of the sample was determined by the Kjeldahl method and an adjacent portion was soaped for 10 min. at 95° C., rinsed, dried, and the nitrogen content estimated in the same way. Both portions were weighed in a bone-dry condition prior to the nitrogen determination. The results obtained are expressed as the percentage loss of nitrogen on soaping.

(ii) *Crease recovery.* Small strips of fabric 1 × 4 cm. were prepared by cutting just over 1 cm. wide and fraying down to correct width. These were folded and placed between glass plates under a weight of about 4 lb. for 3 min. and then floated edgeways on a clean mercury surface for 2 min. to recover from creasing. The strips were finally transferred carefully to paper and the recovery angle marked out, the crease-recovery being then expressed as % chord/diameter. Test results obtained by this method are higher than those given by the T.B.L. method in which the recovery is affected by gravity. An average of six determinations is normally taken as the percentage crease recovery for the sample under test. The results are affected by the time allowed for conditioning after curing the sample and at least 24 hr. were therefore allowed before testing. In the case of viscose rayon, used in some comparative experiments, conditioning appears to be slower and crease recovery was determined after storing for at least 7 days. The results are also influenced by relative humidity, and samples should preferably be tested under standard conditions of temperature and relative humidity. This was not possible in the present case.

(iii) *Tensile strength.* Strips of fabric 5 × 1 in. were pulled in a Goodbrand Tensile Testing machine with constant rate of extension. The strips were prepared by cutting to a width of about 1.1 in. and fraying down to 1 in. The average value for 12 strips was normally taken as the tensile strength.

Wherever possible, samples from one series of related experiments were tested on the same day to minimize the effect of relative humidity. In some experiments wet and oven-dry tensile strengths were also determined. The former were carried out on strips which had been immersed in distilled water for 15 min. before testing and were then lightly pressed between sheets of blotting paper and pulled in the machine. Oven-dry tests were carried out by placing the strips in an oven at 85° C. for 30 min., rapidly transferring to a desiccator and removing one by one for pulling in the machine.

(iv) *Tear strength.* This was determined by use of a dynamic tear tester of the Elmendorf type. Pieces 6.5 × 8 cm. were cut by means of the template provided and torn in the machine. The two halves of each test specimen were then torn again separately in order to obtain three test figures from each specimen. Three test pieces were normally cut from each sample so that nine tear test figures were normally obtained. Although this method of repeated tears on one specimen is not recommended for tear testing of paper where some loss of accuracy occurs, experience has shown it to be satisfactory for fabrics. Wet and oven-dry tear tests were performed on samples previously treated as described for the corresponding tensile tests.

Experimental Work

Comparison of Various Resin Precondensates

In order to compare the results obtained by the application of different resin precondensates, the following types of product were examined:

A. Unmodified methylol-urea precondensate.
(Urea-formaldehyde ratio 1 : 1.5)
B. Unmodified methylol-urea precondensate.
(Urea-formaldehyde ratio 1 : 1.9)
C. Stabilized urea-formaldehyde precondensate.
(Urea-formaldehyde ratio 1 : 1.9)
D. Methylated methylol-urea.
(Urea-formaldehyde ratio 1 : 1.5)
E. Methylated methylol-urea.
(Urea-formaldehyde ratio 1 : 1.7)
F. Methylated methylol-urea.
(Urea-formaldehyde ratio 1 : 1.9)
G. Methylol-ethylene-urea.
H. Methylated methylol melamine.
(Melamine-formaldehyde ratio 1 : 3.3)
I. Methylated methylol melamine.
(Melamine-formaldehyde ratio 1 : 4.8)

The above products were applied to the selected cotton fabric at concentrations of 1, 2, 3, 4, 6, 10, and 14% resin solids. The accelerator employed was 1% ammonium thiocyanate on resin solids with the exception of G. where 2% was used. The samples were padded, dried, and cured, as described above.

After conditioning, the samples were tested for crease recovery, tensile strength, and tear strength, all these properties being measured in the warp direction.

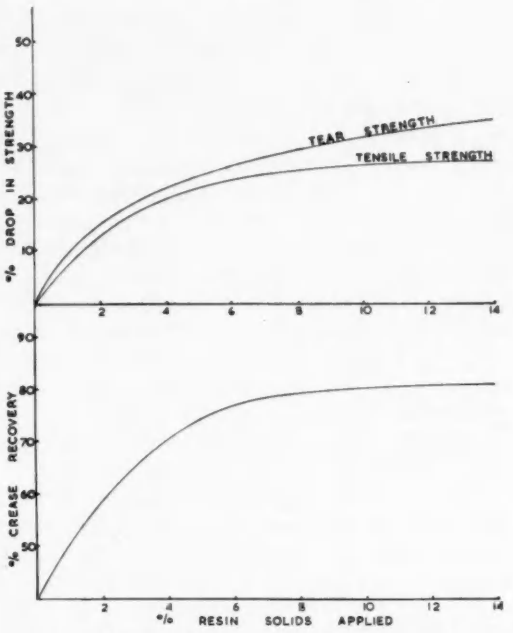

Fig. 1a. Relationship between resin soldis applied to unmercerized cotton and the resultant crease recovery, tensile and tear strengths. (U/F ratio 1:1.5)

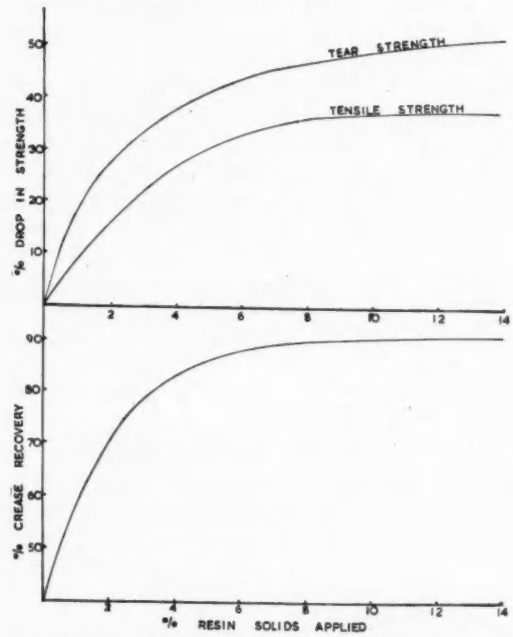

Fig. 1b. Relationships between resin solids applied to unmercerized cotton and the resultant crease recovery, tensile and tear strengths. (U/F ratio 1:1.9)

TABLE I

Product applied	% Resin solids on fabric	% Crease recovery	95% Conf. limits* (+ or −)	% Drop in tensile strength	95% Conf. limits* (+ or −)	% Drop in tear strength	95% Conf. limits* (+ or −)
A	1	53	0.4	8.7	2.4	7.6	1.9
A	2	55	1.8	14.5	2.0	16.2	2.8
A	3	69	0.8	16.1	2.0	18.3	2.1
A	4	66	2.2	19.6	2.0	20.5	2.1
A	6	78	2.6	23.4	0.8	24.3	2.4
A	10	76	1.4	27.0	2.4	31.7	1.7
A	14	79	2.4	24.0	1.4	35.0	1.2
B	1	60	2.8	6.8	2.0	20.0	1.4
B	2	63	3.2	11.8	2.4	27.3	2.8
B	3	76	4.0	21.8	2.0	32.7	1.4
B	4	83	2.8	25.2	1.6	38.2	1.4
B	6	86	1.6	34.8	2.8	43.6	2.8
B	10	92	0.8	35.0	2.0	50.9	1.4
B	14	89	1.6	35.0	1.6	49.1	1.9
C	1	57	1.0	12.5	2.0	12.3	3.1
C	2	73	1.4	21.2	2.2	22.3	1.4
C	3	79	1.6	25.2	1.8	24.4	1.4
C	4	82	1.2	28.8	1.8	30.5	1.9
C	6	86	1.2	34.0	1.6	35.6	1.7
C	10	92	1.4	38.1	2.0	45.4	1.4
C	14	93	0.8	38.1	1.8	45.4	1.9
D	1	51	2.4	11.6	2.2	9.0	2.1
D	2	55	1.2	16.0	1.2	11.1	2.8
D	3	61	1.4	15.9	1.0	16.1	3.8
D	4	62	0.4	21.5	1.6	20.0	2.1
D	6	70	2.6	27.8	3.4	24.4	2.1
D	10	81	1.2	36.8	4.0	31.3	1.7
D	14	79	1.0	28.6	1.8	37.0	1.4
E	1	57	2.0	15.2	1.4	11.7	2.4
E	2	63	1.8	16.7	1.4	19.1	1.7
E	3	68	3.0	22.3	1.4	25.3	1.4
E	4	75	2.0	21.2	1.4	30.5	1.2
E	6	81	0.8	25.3	1.4	34.2	1.7
E	10	86	0.4	25.9	1.0	40.9	1.7
E	14	87	1.4	29.4	2.6	45.0	1.2
F	1	53	2.6	11.6	1.6	14.6	1.9
F	2	63	1.8	18.2	1.8	20.0	2.1
F	3	72	1.6	24.0	2.4	26.1	2.8
F	4	75	0.6	27.7	1.8	32.0	1.4
F	6	80	1.2	27.4	2.2	33.6	1.4
F	10	86	0.4	30.0	1.8	40.9	1.2
F	14	86	2.2	32.3	1.8	44.8	1.4
G	1	58	1.8	16.6	1.4	19.8	3.3
G	2	73	0.4	24.1	1.8	28.0	1.9
G	3	83	1.6	35.7	2.2	34.2	1.7
G	4	88	0.6	35.5	1.2	40.3	0.7
G	6	92	0.8	42.6	1.8	45.3	1.7
G	10	96	0.6	43.0	1.4	50.9	1.2
G	14	96	0.6	42.0	1.2	52.2	1.2
H	1	59	2.4	13.8	2.4	15.8	1.9
H	2	64	1.4	18.0	2.0	22.7	1.4
H	3	71	2.2	19.4	1.6	25.4	1.4
H	4	76	1.4	22.6	2.6	30.1	2.1
H	6	83	1.4	27.6	1.8	35.4	2.1
H	10	85	1.4	29.4	1.6	41.1	1.7
H	14	90	0.6	32.9	1.4	45.7	1.9
I	1	55	0.6	10.3	2.0	12.7	1.9
I	2	61	1.0	15.7	1.4	22.4	2.1
I	3	63	3.0	19.6	1.6	27.8	1.7
I	4	76	1.0	27.6	1.8	32.5	2.1
I	6	75	1.6	31.5	2.2	40.1	1.4
I	10	87	1.2	40.8	1.2	45.6	1.9
I	14	89	1.2	41.0	1.6	51.6	1.4

* The 95% confidence limits were calculated from the range of observations by the method of Dean and Dixon [*Anal. Chem.* **23**, 636 (1951)].

The results are summarized in Table I, which shows the crease recovery obtained and the percentage drop in tensile and tear strength compared with the untreated fabric.

Comments:

1. The effects produced, crease recovery, drop in tensile strength, and drop in tear strength are not directly proportional to the resin solids applied. The relationship is shown in Figures 1*a* and 1*b* for two specific examples (Products A and B).

2. The percentage crease recovery and percentage drop in tensile and tear strengths at a given applied solids content are dependent on the urea/formaldehyde ratio in the case of U/F precondensates, being greater as the proportion of formaldehyde is increased. (This relationship is evident if Figures 1*a* and 1*b* are compared.)

3. The drop in tensile or tear strength is directly proportional to the crease recovery imparted regardless of the type of precondensate employed. This is illustrated in Figures 2*a* and 2*b* in which lines have been drawn based on calculation of the regression equation from the results obtained. The 5% standard error limits were determined by use of "Student's *t* value."

Effect of Mercerization

In order to examine the effect of mercerization on fabric strength after resin treatment, a plain weave 55 × 45 cotton fabric was employed. Samples of this fabric unmercerized, semi-mercerized, and fully mercerized were treated at concentrations of 4 and 10% with resin precondensate F (methylated methylol-urea) and the crease recovery, tensile and tear strengths were measured. The results are summarized in Table II, which also includes figures for the percentage crystallinity of the cellulose determined by the iodine absorption method of Hessler and Power [12].

Comments:

Mercerization has clearly effected an improvement in the tensile and tear strengths after resin treatment although the difference between semi- and fully-mercerized fabrics is relatively small.

Effect of Washing Off

It has frequently been emphasized that washing off of resin-treated fabrics is desirable to avoid the danger of after-odors, but little information has been published regarding the effect of this process on fabric strength. In order to obtain some data on this point, a number of resin-treated fabric samples chosen at random have been tested for crease recovery, tensile strength, and tear strength both before and after washing off, the results being summarized in Table III.

Comments:

The following effects of washing off can be observed:

1. The crease recovery appears to be adversely affected in the lower range of values (below 75% recovery) but not if the original crease recovery was over about 85%.

TABLE II

Fabric used	% Resin solids applied	% Crease recovery	Tensile strength (lb.)	% Drop in tensile strength	Tear strength (Elmendorf units)	% Drop in tear strength	Percentage crystallinity of cellulose
Unmercerized	None	52	66.2	—	124*	—	89
Unmercerized	4	80	41.5	37.3	57	54.0	—
Unmercerized	10	86	34.7	47.6	46	62.9	—
Semimercerized	None	47	61.9	—	127*	—	77
Semimercerized	4	71	49.0	20.9	79	37.8	—
Semimercerized	10	85	44.5	28.1	62	51.2	—
Fully mercerized	None	57	64.9	—	145*	—	74
Fully mercerized	4	74	54.0	16.8	87	40.0	—
Fully mercerized	10	84	49.5	23.8	69	52.4	—

* The untreated fabrics were too strong to tear on the Elmendorf machine, and the values given were obtained by doubling figures for half the length of tear.

2. The drop in tensile strength is usually increased.

3. The drop in tear strength is noticeably decreased.

Effect of Curing Conditions

An investigation of the effect of varying the degree of cure of the resin on the results obtained has been carried out. The accelerator employed was ammonium thiocyanate as before, but the degree of cure was varied by alterations in the concentration of catalyst employed or in the curing temperature, the time of cure being maintained at 10 min. as before. Two resin precondensates were examined (C and F) and the crease recovery, tensile and tear strengths were determined as before. The results are summarized

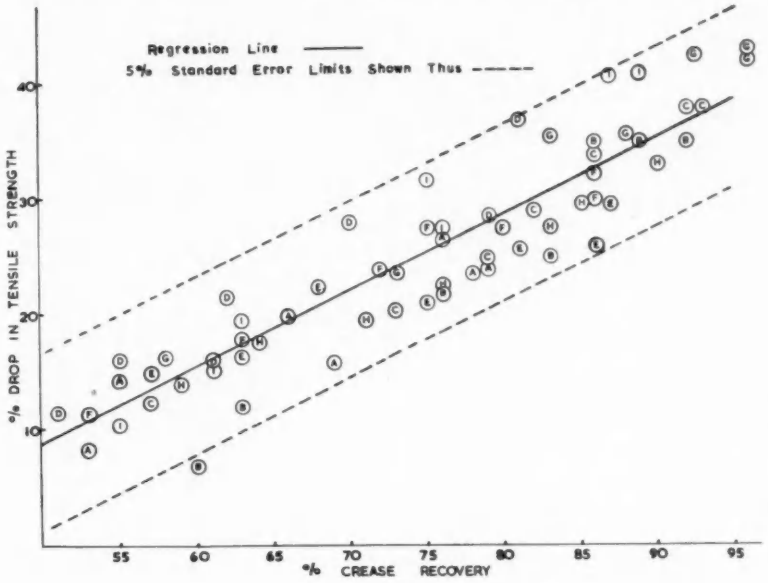

Fig. 2a. Relationship between crease recovery and tensile strength of resin-treated cotton fabric.
Regression equation:

$$y = 0.682\,x - 1.76$$

where
$x = R - 50$ (R = % crease recovery from Table I)
$y = S - 10$ (S = % drop in tensile strength from Table I)
Correlation coefficient $r = 0.9264$

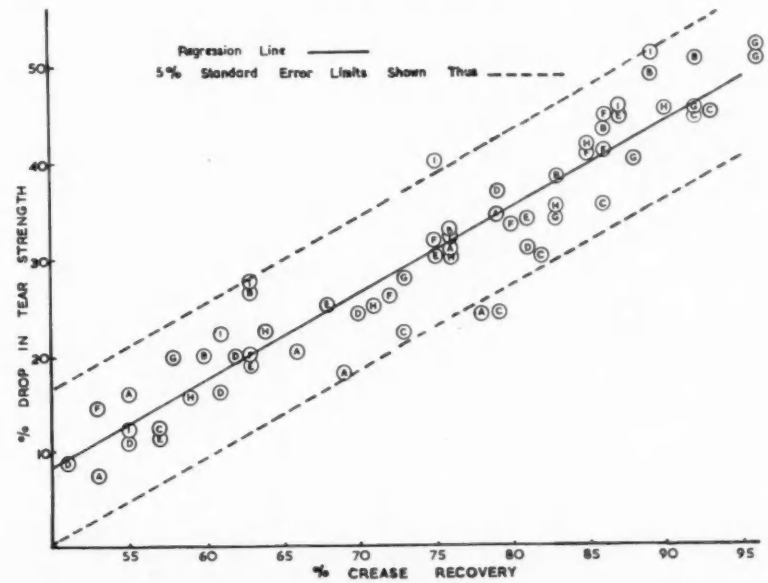

Fig. 2b. Relationship between crease recovery and tear strength of resin-treated cotton fabric.
Regression equation:

$$z = 0.905\,x - 1.80$$

where
$x = R - 50$ (R = % crease recovery from Table I)
$z = T - 10$ (T = % drop in tear strength from Table I)
Correlation coefficient $r = 0.9260$

TABLE III

Sample no.	% Crease recovery		% Drop in tensile strength		% Drop in tear strength	
	Un-washed	Washed off	Un-washed	Washed off	Un-washed	Washed off
1	68	60	15	28	29	21
2	80	65	27	30	36	26
3	88	81	34	37	41	35
4	89	86	38	42	42	38
5	86	84	39	43	43	39
6	91	93	46	47	51	44
7	91	91	45	43	47	42
8	89	93	44	43	45	41
9	88	92	38	41	43	38
10	85	90	34	39	39	36
11	88	89	34	37	34	34
12	87	85	34	36	43	34
13	80	76	26	28	33	24
14	72	73	20	28	25	19
15	59	57	9	13	12	3
16	86	92	44	46	47	41
17	88	89	35	43	39	35
18	79	80	26	38	30	25
19	56	51	13	26	15	6
20	90	94	37	43	44	40
21	85	93	31	37	36	32
22	82	89	26	33	30	26
23	63	65	13	22	15	7
24	91	93	40	42	52	45
25	91	92	37	39	46	40
26	85	89	30	32	42	35
27	79	82	25	26	36	27
28	90	93	40	46	52	44
29	85	93	38	41	48	37
30	85	83	32	41	43	34
31	73	50	20	23	33	15
32	87	87	30	38	38	31
33	90	92	29	38	43	38
34	73	61	21	21	22	13
35	92	89	38	42	45	37
36	64	58	18	18	23	12
37	85	81	29	35	41	32
38	63	59	18	25	20	16
39	86	84	30	38	41	36
40	55	44	16	22	11	6
41	81	78	37	38	31	31
42	61	52	16	26	22	12
43	87	86	41	39	46	40
44	73	69	24	31	28	23
45	96	96	43	46	51	47
46	55	51	15	24	16	2
47	76	69	27	32	32	26
48	63	56	17	16	19	14
49	86	84	26	30	41	33
50	70	64	22	25	22	14

TABLE IV

Resin used	% Ammon. thiocyanate on solids	Curing temp. (° C.)	% Nitrogen loss on soaping	% Warp crease recovery		% Drop in warp tensile strength		% Drop in warp tear strength	
				Unwashed	Washed off	Unwashed	Washed off	Unwashed	Washed off
C	0.1	140	63	61	51	14.6	24.8	26.2	16.4
C	0.2	140	48	68	60	15.4	27.8	28.8	20.8
C	0.5	140	21	80	65	26.6	30.4	36.1	26.2
C	1.0	140	10	88	81	34.0	36.6	41.2	34.8
C	2.0	140	11	89	86	38.0	42.4	41.5	38.4
C	5.0	140	12	86	84	38.6	43.2	42.6	39.3
C	1.0	160	4	91	93	46.4	47.4	50.8	43.8
C	1.0	150	6	91	91	44.6	42.8	47.3	42.3
C	1.0	140	—	89	92	44.0	43.4	45.0	40.8
C	1.0	130	9	87	92	38.0	40.6	43.0	38.1
C	1.0	120	—	85	90	34.4	39.2	39.0	35.7
C	1.0	110	10	87	89	33.6	37.4	34.4	33.9
C	0.5	155	9	87	85	34.2	36.2	43.2	34.2
C	0.5	140	26	80	76	25.6	28.2	33.0	24.4
C	0.5	125	48	72	73	20.4	27.6	25.0	19.3
C	0.5	110	86	59	57	9.2	13.2	11.7	2.5
F	1.0	155	4	91	93	40.4	42.4	51.7	45.0
F	1.0	140	7	91	92	36.6	38.8	46.3	39.9
F	1.0	125	10	85	89	29.6	31.6	42.1	34.6
F	1.0	110	23	79	82	24.8	26.0	36.4	26.6

in Table IV in which, as a measure of degree of cure, the % loss of nitrogen on soaping for 10 min. at 95° C. is also given. Ten per cent resin solids were applied to the fabric in each case.

Comments:

The linear relationship between crease recovery imparted and drop in tensile or tear strength appears to hold good regardless of the degree of cure.

Effect of Degree of Condensation of Resin Used

It has been stated in the introduction to this paper that the resin precondensate used for crease-resist finishing must be of low molecular size so as to penetrate the cellulose fibers. In order to examine the effect of degree of condensation, a stabilized urea-formaldehyde precondensate was prepared and the solution was heated under reflux. Samples were taken at intervals and applied to both cotton and rayon fabrics. The samples were all applied at the same concentration (10% resin solids on fabric) and 1% ammonium thiocyanate on resin solids was employed as accelerator. The impregnated fabric was air-dried and cured by the standard method and tested for crease recovery, tensile and tear strength, while an estimate of the handle after treatment was also made. The results are summarized in Table V.

TABLE V

Sample no.	Reflux time (hr.)	Estimate of fabric handle		% Crease recovery		% Change in tensile strength		% Change in tear strength	
		Cotton	Rayon	Cotton	Rayon	Cotton	Rayon	Cotton	Rayon
1	2	Soft	Soft	94	90	−28.1	Nil.	−46.9	−35.5
2	2¾	Soft	Soft	94	87	−28.5	− 2.5	−48.2	−28.1
3	3¼	Soft	Soft	94	84	−29.2	+ 5.4	−48.2	−25.5
4	4½	Soft	Full	93	78	−27.0	+ 3.8	−46.3	−22.8
5	7½	Soft	Rather stiff	91	67	−20.2	− 9.7	−43.2	−21.7
6	9¼	Firm	Stiff	91	49	−25.2	−46.1	−47.8	−72.8
7	11	Stiff	Very stiff	84	45	−20.7	−55.3	−53.1	−76.2

TABLE VIa. Effect on Tensile Strength

Resin used	Fabric used	Oven dry tensile strength (lb.)	% Change on untreated	Normal dry tensile strength (lb.)	% Change on untreated	Wet tensile strength (lb.)	% Change on untreated
Untreated	Cotton	39.5	—	51.3	—	52.8	—
Untreated	Rayon	69.0	—	55.0	—	29.0	—
C	Cotton	30.1	−23.8	36.1	−29.6	33.6	−36.4
C	Rayon	69.2	+ 0.3	55.4	+ 0.7	33.9	+16.9
F	Cotton	28.1	−28.9	32.3	−37.0	31.0	−41.3
F	Rayon	62.5	− 9.4	51.8	− 5.8	31.9	+10.0

TABLE VIb. Effect on Tear Strength

Resin used	Fabric used	Oven dry tear strength Elmendorf units	% Change on untreated	Normal dry tear strength Elmendorf units	% Change on untreated	Wet tear strength Elmendorf units	% Change on untreated
Untreated	Cotton	48.7	—	57.0	—	72.1	—
Untreated	Rayon	87.4	—	78.0	—	27.5	—
C	Cotton	33.2	−31.8	34.9	−38.8	34.4	−52.3
C	Rayon	63.9	−26.9	55.4	−29.0	31.1	+13.1
F	Cotton	25.7	−47.8	30.9	−49.0	32.8	−54.5
F	Rayon	56.5	−35.4	43.0	−44.9	29.4	+ 6.9

TABLE VII

Thermoplastic copolymer used and % solids	% Melamine formaldehyde solids	Estimate of handle	% Crease recovery	% Drop in tensile strength	% Drop in tear strength
None	10.0	Soft	85	29.4	41.1
None	6.0	Soft	83	27.6	35.4
None	3.0	Soft	71	19.4	25.4
J 3.0	7.0	Slightly firm	76	26.4	36.7
J 7.0	3.0	Slightly firm	72	14.0	28.5
K 3.0	7.0	Slightly stiff	81	28.6	36.5
K 7.0	3.0	Stiff & leathery	71	19.6	40.3
L 2.0	8.0	Fairly stiff	69	14.4	32.7
L 3.0	7.0	Stiff & papery	73	15.6	37.6
L 5.0	5.0	Stiff & papery	63	11.4	43.3
L 7.0	3.0	Stiff & papery	51	3.6	26.0
M 3.0	7.0	Slightly rubbery	83	25.4	24.2
M 7.0	3.0	Slightly rubbery	69	14.2	9.6
N 3.0	7.0	Stiff & leathery	79	21.2	31.8
N 7.0	3.0	Stiff & leathery	52	2.2	11.8

The thermoplastic materials used were as follows:

J. Styrene/ethyl acrylate copolymer.
K. Butyl methacrylate/ethyl acrylate copolymer.
L. Vinyl acetate/ethyl acrylate copolymer.
M. Butadiene/acrylonitrile copolymer.
N. Styrene/vinyl acetate copolymer.

Comments:

It is clear that a more highly condensed resin precondensate is still capable of penetrating the interior of cotton fibers, but not of rayon fibers. As condensation proceeds, the effect of the resin precondensate on the tensile strength of rayon changes adversely, while the effect on the strength of cotton remains approximately constant.

Influence of Moisture Content of Fabric on Strength

It is known that the wet strength of cotton fabrics is higher than the dry strength, while the reverse is true for viscose rayon. In order to examine the effect on these relationships of resin treatment, two types of precondensate (C and F) were applied to standard cotton and rayon fabrics at a concentration of 10% resin solids using 1% ammonium thiocyanate on resin solids as accelerator and curing under normal conditions. Tensile and tear strength tests were carried out under normal conditions (about 60 to 65% R.H.) and also oven dry and wet as specified above. The results obtained are shown in Tables VI*a* and VI*b*.

Effect of Thermoplastic Additives

(a) *Copolymer emulsions.* Various thermoplastic copolymer emulsions have been suggested in the literature as additives to the crease-resist bath when treating cotton fabrics. A large number of such materials have been examined, most of which adversely affected the handle of the fabric. Some improvement in tensile strength could usually be obtained, but this was frequently accompanied by a drop in tear strength. The various thermoplastic additives were tested in conjunction with a methylated methylol melamine precondensate (H). The thermoplastic and melamine resin components were applied in various proportions, the total resin solids on the fabric being maintained at 10%. Ammonium thiocyanate was again employed as accelerator. The various formulations were applied to the standard cotton fabric and the crease recovery, tensile and tear strengths of the treated samples were determined. A number of examples showing the variety of results obtained has been selected, and the test results are summarized in Table VII.

Comments:

The results obtained are varied. Materials J and K improve tensile strength, but not tear strength. L improves tensile strength, but only at the expense of crease recovery. M and N improve both tensile and tear strength but N does so at the expense of crease recovery. M would appear therefore to offer at least a partial solution to the problem, but the handle of the fabric is rather rubbery and might be described as lifeless, so that it would probably be unacceptable commercially. Furthermore, butadeine/acrylonitrile copolymers tend to yellow at the temperatures employed for the baking process.

(b) *Polyvinyl alcohol.* The use of amino-resin precondensates in conjunction with polyvinyl alcohol to improve fabric strength has been advocated both for crease-resisting cellulosic fabrics and for durable mechanical finishing. A number of formulations based on various amino-resin precondensates with and without polyvinyl alcohol additions have therefore been examined. They have been applied to cotton fabric, and the treated samples have been tested for crease recovery, tensile and tear strengths as before. Table VIII gives a summary of the results obtained, the amino-resin precondensates being designated C, G, and H, as previously described.

TABLE VIII

% Polyvinyl alcohol applied	Amino resin used and % applied	% Crease recovery	% Drop in tensile strength	% Drop in tear strength
None	C 4.0	79	36.4	37.6
1.0	C 4.0	75	32.0	42.7
2.0	C 4.0	—	32.0	48.5
None	G 4.0	88	45.2	38.5
0.5	G 4.0	—	42.4	43.6
1.0	G 4.0	88	42.0	55.8
2.0	G 4.0	80	37.0	57.8
None	H 4.0	77	34.4	35.8
0.5	H 4.0	70	31.0	37.3
1.0	H 4.0	76	32.0	42.2
2.0	H 4.0	69	30.0	51.1

Comments:

Polyvinyl alcohol clearly improves the tensile strength of the treated fabric, but adversely affects the tear strength. Even at 0.5% the polyvinyl alcohol has a noticeable stiffening effect on the fabric.

Effect of Softeners

The use of various softening agents, particularly those of the cationic type, either as additives to the

amino-resin bath or as an aftertreatment has frequently been advocated and an improvement in the strength of crease-resisted cellulosic fabrics has been claimed. Durable water repellents such as a stearamide-modified melamine resins have similar properties, and it has been suggested that addition of such materials to the crease-resist bath will not only give a durable crease-resistant, showerproof, and stain-resistance cotton of improved handle, but also will improve the fabric strength. A product of this type has been tested at various concentrations in conjunction with a precondensate of the methylated methylol-urea type (Reference F above). The formulations were applied to the standard cotton fabric and tested for crease recovery, tensile and tear strengths both before and after washing off. Table IX gives a summary of the results obtained.

Comments:

1. The addition of the water repellent has effected some improvement in crease recovery.
2. The tear strength has been improved to some extent, but the tensile strength has been adversely affected.
3. After washing off, the tensile and tear strengths remain substantially unaltered, so that they are comparable with the tensile and tear strengths of the washed-off material containing no water repellent.

Effect of Fabric Construction

All the work on unmercerized cotton previously described has been carried out on one fabric, an 80 × 80 plain weave material of about 3½ oz. to the square yard. The results obtained show a considerable drop in both tensile and tear strengths on resin treatment which would appear difficult to reconcile with the numerous claims in recent years that crease-resistant cottons could be produced without serious loss of strength. The importance of fabric construction has been pointed out in several discussions on the crease-resisting of cellulosic fabrics [5, 6, 10], and a number of fabrics of varied construction have therefore been examined to assess the significance of this point. A range of commercially available fabrics were scoured to remove the normal nondurable finish and were each treated with the same series of resin formulations, one of which contained an addition of polyvinyl alcohol since it was thought that this additive might be of advantage on some fabric constructions only.

TABLE X

Fabric no.	Description	Construction	
	White		
1	Lawn	86 × 80	80/120's
2	Poplin	118 × 60	2/80's/40's
3	Shirting	56 × 52	18/16's
	Dyed		
4	Poplinette	98 × 62	32/30's
5	Poplin	123 × 67	38/40's
6	Limbric	63 × 85	52/32's
7	Cashmere	56 × 80	36/28's
8	Imitation linen	46 × 46	13/13's
9	Khaki drill	96 × 48	16/12's
10	Khaki jean	56 × 80	36/24½'s
11	Worsted border cashmere	72 × 100	36/26's
12	Sateen	71 × 84	32/30's

TABLE IX

% Water-repellent applied	% Resin precondensate F applied	% Crease recovery		% Drop in tensile strength		% Drop in tear strength	
		Unwashed	Washed off	Unwashed	Washed off	Unwashed	Washed off
None	5.0	87	87	29.8	38.4	38.3	31.4
1.0	5.0	93	88	33.8	37.6	30.0	28.5
3.0	5.0	95	90	38.4	40.2	30.7	30.5
5.0	5.0	94	92	37.8	37.2	32.5	30.9
None	10.0	90	92	28.8	38.4	42.5	37.6
1.0	10.0	98	94	41.4	41.6	37.1	36.5
3.0	10.0	96	96	43.8	41.4	38.2	37.4
5.0	10.0	97	98	41.8	40.8	39.3	38.2
1.0	None	63	55	15.0	19.8	2.2	1.3
3.0	None	66	62	24.8	25.4	10.2	10.5
5.0	None	79	69	26.6	27.2	16.5	14.9

TABLE XI

Fabric no.	Resin used	% Warp crease recovery	% Drop in tensile strength		% Drop in tear strength	
			Warp	Weft	Warp	Weft
1	C	92	46	46	—	68
1	F	97	43	38	—	67
1	F+PVA	91	25	—	—	42
1	H	88	37	—	—	54
2	C	86	14	38	35	45
2	F	88	18	30	41	49
2	F+PVA	70	17	27	37	47
2	H	78	11	30	32	52
3	C	87	38	31	45	51
3	F	94	37	29	45	47
3	F+PVA	85	31	28	42	48
3	H	85	31	36	44	50
4	C	91	31	39	38	46
4	F	94	25	29	41	42
4	F+PVA	81	23	24	31	48
4	H	81	21	—	37	36
5	C	92	24	41	42	36
5	F	93	29	27	47	35
5	F+PVA	74	22	24	38	48
5	H	82	15	32	39	41
6	C	88	16	27	16	23
6	F	91	16	17	21	33
6	F+PVA	76	19	16	14	37
6	H	87	10	21	12	19
7	C	88	28	32	19	36
7	F	95	17	25	23	36
7	F+PVA	85	4	32	28	43
7	H	86	7	29	15	38
8	C	89	45	41	40	53
8	F	89	38	36	40	57
8	F+PVA	86	34	34	38	59
8	H	88	36	48	38	65
9	C	92	47	—	—	65
9	F	94	42	—	—	63
9	F+PVA	83	48	—	—	56
9	H	89	44	—	—	56
10	C	89	29	27	27	28
10	F	78	19	12	22	20
10	P+PVA	65	16	13	20	27
10	H	80	20	19	20	28
11	C	84	21	—	42	—
11	F	82	10	17	38	—
11	F+PVA	90	8	13	23	—
11	H	80	20	—	29	—
12	C	84	1	—	36	32
12	F	86	−2.5	−2	36	22
12	F+PVA	79	−6	−3	29	—
12	H	88	1	—	20	14

N.B. A minus sign denotes an increase in strength.

TABLE XII

Fabric no.	% Warp crease recovery		% Drop in tensile strength		% Drop in tear strength	
	Untreated	Treated	Warp	Weft	Warp	Weft
1	52	92	42	42*	—	63
2	48	84	15	33	36	49
3	47	89	35	32	45	49
4	48	89	26	34*	39	41
5	52	89	23	33	43	37
6	54	89	14	22	16	25
7	54	90	17	29	19	37
8	45	89	40	42	39	58
9	58	92	44	—	—	61
10	61	82	23	19	23	25
11	68	82	17	—	36	—
12	76	86	Nil.	—	31	23

* Averages of two resin treatments only.

The resin precondensates C, F, and H were again employed. They were applied so as to give 10% resin solids on the fabric, and F was also tested in conjunction with 0.5% polyvinyl alcohol on fabric weight. Particulars of the fabrics examined and details of their construction are listed in Table X.

The results of tests for crease recovery, tensile and tear strengths on the treated fabrics are summarized in Table XI. Tensile and tear strengths were determined in both warp and weft directions in most cases. The samples were not washed off.

The behavior of fabrics of different construction varies considerably, as shown by the above figures, but the differences between one resin treatment and another when applied to the same fabric are relatively small. If we take average figures for the three resin treatments, excluding that involving polyvinyl alcohol, since it introduces another factor, we obtain the results shown in Table XII, where the crease recovery of the untreated fabric is also shown for comparison.

It is clear that Fabric No. 6 gives superior results, while No. 10 shows some promise, although the crease recovery imparted is not outstanding. It should be emphasized that the amount of resin solids applied (10%) is greater than would normally be recommended for a cotton fabric, but this quantity was chosen in much of the work described in this paper in order to render the conditions more critical. It must be made clear that the above series of fabrics were chosen as being commercially available and since their past history is unknown, the results obtained must be regarded with some caution. Nevertheless, there would appear to be sufficient evidence to suggest that suitable choice of fabric construction has a profound effect on the strength of the crease-resisted material.

It was felt that the average effect of various precondensates over a range of fabrics might be of some interest, and for this purpose eight fabrics were selected from the above range on which test results are complete, except for the weft tensile strength on sample No. 4 for one resin treatment. The average values for crease recovery and for tensile and tear strength, both warp and weft, have been calculated for Fabrics 2 through 8, and 10 for each resin treatment and are given in Table XIII.

TABLE XIII

	Percentage			
	C	F	F+PVA	H
Warp crease recovery	89	90	78	83
Drop in strength				
warp tensile	28	25	21	19
weft tensile	35	26	25	31
warp tear	33	35	31	30
weft tear	40	40	45	41

These figures would suggest that polyvinyl alcohol can produce only a slight improvement in tensile strength at the expense of crease recovery imparted, while a similar result is obtained by employing a less effective crease-resisting medium, such as melamine-formaldehyde precondensate. In two cases, sample Nos. 1 and 11, the polyvinyl alcohol appears to have effected some improvement in fabric strength without loss of crease recovery.

General Conclusions

The work described in this paper leads to the following general conclusions:

1. The drop in tensile or tear strengths resulting from a crease-resisting treatment of cotton is directly proportional to the crease resistance imparted, regardless of the type of precondensate applied.

2. The degree of crease recovery imparted by a certain concentration of resin solids varies considerably from one type of precondensate to another, the order of efficiency being

(a) Ethylene-urea formaldehyde (most efficient)[1]
(b) Urea-formaldehyde
(c) Melamine-formaldehyde

The efficiency of urea-formaldehyde precondensates increases with higher urea-formaldehyde ratios. Methylation of the precondensate improves its bath stability but has little effect on the results obtained on application to cotton. The degree of condensation of the precondensate has little effect over a quite considerable range when applied to cotton, but on rayon the more condensed products have an adverse effect on handle and crease recovery imparted.

3. Washing off appears to improve the tear strength of treated cotton but has an adverse effect on tensile strength.

4. Thermoplastic additives improve tensile strength to some extent, but generally have an adverse effect on tear strength.

5. Softeners appear to have an effect similar to washing off.

6. Mercerization of cotton has a beneficial effect on its behavior after crease-resisting.

7. Fabric construction plays an important part in its strength after resin treatment.

Discussion

It is hoped in the following paragraphs to put forward a rational explanation of the observed results in accordance with the known properties of cellulosic materials.

Let us consider first the construction of the fabric. The tensile strength as measured on a strip of fabric 1 in. wide is substantially a measure of the yarn strength, which in turn depends on two factors, yarn twist and fiber strength. If the fiber is strong and the twist low, breakage will tend to occur by slipping of the fibers, while if the twist is high and the strength of the fiber reduced by resin treatment, fiber breakage may occur before slipping. The presence of a small but unavoidable quantity of resin on the surface of the fibers will tend to increase strength by fiber-bonding or increase of the coefficient of friction between fibers, and washing off will reduce this tendency and might be expected to result in a lower tensile strength. It is clear, therefore, that the yarn twist will affect the drop in tensile strength of a specific cotton fabric produced by resin treatment.

Tear strength is even more dependent on fabric construction. It depends on distortion of the fabric structure at the point of tearing as well as on the properties of the yarn. For this reason the application of stiffened finishes, such as starch, will considerably reduce tear strength. Removal of stiffening agent by washing will improve tear strength, and in a similar way an improvement will be obtained on washing off, which removes traces of surface resin. The resistance of a fabric to tearing is thus affected by the type of weave and the spacing of the yarns as well as the yarn twist.

To summarize these points, it is suggested that the strength of a cotton fiber is lowered to a constant extent by the application of a certain quantity of a specific amino-resin precondensate. The tensile and tear strength of a specific cotton fabric after resin treatment are then dependent in certain ways on its construction. There may be differences in behavior of different types of cotton on resin treatment, while fiber length may also be involved, but these points have not been investigated.

Let us now consider the effect of the resin on the cellulose. It has been stated that the principal requirement is that the resin precondensate should be of low molecular size so as to enable it to penetrate the amorphous regions of the cellulose. Molecules of larger size will not penetrate the fibers and will result in stiffening of the fabric and loss of crease-resistance. Since it has been established that more highly condensed resins will still impart crease-resisting properties to cotton fabrics but not to viscose rayon, it follows that the spaces through which the precondensate molecules enter the fiber, the voids in the amorphous regions, must be larger in cotton than in viscose rayon.

The mechanism whereby resistance to creasing is imparted to cellulosic fabrics is not completely clear but would appear to be associated with the increase in elasticity (Young's modulus) which has been ob-

[1] It should be appreciated that the most efficient crease-resisting agent may not be the best to use in practice, its successful application being necessarily more critical.

served and which would increase the resistance of the fiber to deformation. This increased elasticity is associated with a decrease in extensibility. These effects have been explained as due to filling of the amorphous regions with a three-dimensional resin network or to chemical cross-linking of the cellulose [7]. Borghetty and Fornelli [5] have claimed that the work of Gagliardi [9] on alkaline catalysts for the reaction establishes that crease recovery can be imparted to cotton under conditions where cross-linking of the cellulose is impossible. A recent paper by Murakami and co-workers [14] states, however, that alkaline catalysts of the type employed by Gagliardi are really "latent acid catalysts," the mechanism being a Canizzaro reaction with the free formaldehyde present. This seems probable, since the catalysts are effective only with methylol urea precondensates, which normally contain considerable percentages of free formaldehyde. Steele and Giddings [17] have asserted that the cross-linking mechanism is more effective in crease-resisting cotton but not in the case of rayon.

It is clear that the matter is extremely controversial and both the suggested mechanisms are probably involved, but it is of interest to note that the most efficient crease-resisting agents (methylol ethyleneureas) appear to be incapable of forming a three-dimensional network, so that in this case at least cross-linking would seem to be of major importance. Melamine-formaldehyde precondensates which are capable of forming the most complex three-dimensional network are less effective agents for crease-resisting cellulose.

It has been previously suggested [16] that a theoretical explanation of the observed effects of crease-resist treatments on the tensile strength of cellulosic fabrics may be reached by assuming that the crystalline regions of the fiber are reduced in strength by resin treatment, while the amorphous regions are increased in strength. The composite effect over the whole fiber is thus dependent on the proportions of crystalline and amorphous cellulose, and since regenerated cellulose contains a higher proportion of amorphous material, the result could be an over-all increase in strength, while in cotton an over-all decrease could occur. It was realized at the time that this was an oversimplification of the problem, but it was useful as a working guide and appeared to explain the improvement in results obtained by mercerization of cotton. It does not explain the loss of tensile strength which occurs in washing off treated cotton fabrics or the corresponding increase in tear strength. Recent published information suggests a starting point from which a more rational explanation can be evolved. Meredith [13] has considered the wet and dry strength of natural and regenerated cellulose fibers. He states

> In flax and Fortisan the degrees of crystallinity and molecular orientation are high, so that they show low extension at break and no slipping of the long molecules which are securely anchored in the crystallites. Cotton shows a higher breaking extension because the chain molecules spiral round the fibre axis at an angle of about 30° and the elongation of the spiral contributes to the extension. However, the fibre still breaks with a snap because the long chain molecules passing through the amorphous regions are secured in the crystalline regions by the cooperative effort of large numbers of secondary bonds and the chain molecules break before they slip. With ordinary viscose rayon the molecular orientation is low except for the surface layers which are more highly oriented. This means that the molecules in the surface layers are fully aligned at low extension and begin to slip whilst the molecules in the core start to swing into alignment with the fibre axis. As more and more molecules become orientated, it becomes harder to extend the fibre but this process does not proceed very far owing to the relatively short chain length which provides poor anchorage in the crystalline regions and so the molecules slide past each other and the fibre breaks.
>
> Since nearly all textile fibres absorb water, the mechanical properties depend on the relative humidity of the surrounding air and controlled atmospheric conditions are necessary for measuring these properties. Native cellulose fibres such as cotton usually increase in strength with increase in relative humidity, whereas artificial and protein fibres decrease in strength. The decrease in strength of rayons is ascribed to the penetration of water molecules which weakens the lateral cohesion on which their strength depends. The increase in strength of native cellulose fibres like cotton, flax and hemp, is due to the water in the amorphous regions acting as a lubricant, releasing internal stresses in the long chain molecules anchored to the crystalline regions and, so increasing the fibre strength by a more uniform distribution of stress. It is interesting to note that the strength of highly tendered cotton decreases with increase in relative humidity in a similar way to rayon, and this is probably due to the breaking of the chain molecules in the amorphous regions during tendering, which leaves little internal stress to be released by the lubricating action of the water.

He further points out that the extension at break increases with relative humidity for all fibers and the Young's modulus decreases considerably as the adsorbed water reduces the cohesion of the chain molecules in the amorphous regions.

Let us consider how these points may be used to offer an explanation of the behavior of crease-resisted cellulosic fibers. It is known that crease-resist treatments reduce the water absorption of cellulose and its solubility in solvents. They also increase the Young's modulus and reduce the extensibility. In these ways, they are clearly acting in the opposite way to absorbed water, and if their behavior is interpreted in all respects as opposite to that of water, all the effects on fabric strength can be explained. In native cellulose fibers, the resin network or series of cross-links in the amorphous regions prevents the release of internal stresses in the long chain molecules and so reduces fiber strength. In regenerated cellulose, the penetration of water into the amorphous regions which weakens lateral cohesion is prevented and any cross-linking which takes place will increase the effective molecular chain length and with it the strength of the fiber. These effects are more noticeable under conditions of high humidity as would be expected.

It is concluded, therefore, that the changes in strength of cellulosic fabrics on resin treatment are independent of the nature of the precondensate applied, provided that the molecular size is small enough to permit penetration of the amorphous regions, although the effectiveness as crease-resisting agents may vary from one precondensate to another. This difference in behavior may be due to the varying tendency to cross-link the cellulose rather than form a three-dimensional resin network in the amorphous regions.

With cotton, the loss in strength may be improved somewhat by mercerization. The use of thermoplastic materials or softeners as additives to the resin bath usually results in the improvement of one property of the treated fabric at the expense of another.

It is clear that choice of a fabric of suitable construction may have a profound effect in reducing the loss of strength following resin treatment, while the processing conditions should clearly be chosen so as to minimize the effects of migration leading to the deposition of surface resin.

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Experimental Study of the Viscoelastic Properties of Textile Fibers

Part II: The Influence of Physical Treatments upon the Dynamic Properties of Some Fiber-Forming Polymers

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Introduction

In a previous paper of this series [24], viscoelastic behaviors of some commercial textile fibers were measured, using several longitudinal-vibration methods, at a standard air condition, 20° C. and 65% R.H., over a range of frequency from subsonic to supersonic, and the results were represented in terms of the so-called "relaxation spectrum" over a range of relaxation time from 1×10^{-6} to 1 sec. It was found that the spectrum obtained showed a remarkable contrast to those obtained for rubberlike materials over the same relaxation time range under similar experimental conditions.

The relaxation spectrum of textile fibers can be approximated well by the so-called "box-type distribution," having almost constant intensity of about 10^9 to 10^{10} dyne/cm.^{2} over the relaxation time range mentioned above, while those of rubberlike materials, such as polyisobutylene [2, 18, 23, 40, 50, 58], GR-S [5, 32], and butyl rubber [16, 32], over the same relaxation time range are by the so-called "wedge-type distribution," followed by a box-type distribution which has much lower intensity than that obtained in textile fibers. The slope of the wedge appears to be decreased when the nature of the test materials is changed from a rubberlike to a glasslike or a highly oriented crystalline one.

The relaxation spectrum is indeed a mathematical representation which can conveniently describe the linear viscoelastic behavior of materials and is nothing but a phenomenological function having few essential parameters. Therefore, the difference between the types of relaxation spectra mentioned above may not be directly interpreted in terms of molecular constitutions. However, it does enable us to establish a systematic and natural formulation of the laws of viscoelastic behavior, and must be a characteristic function of a given material in the sense that it represents a distribution of relaxation mechanisms corresponding to various modes of cooperative motions of the molecule constituting the material against external mechanical excitations.

For several amorphous polymers and for concentrated polymer solutions, some molecular aspects of the relaxation spectrum have been clarified through experiments dealing with the effects of molecular weight [1, 2, 8, 21, 41, 46, 59], chemical composition of polymer [4, 11, 19, 20], presence and nature of added diluent [14, 15, 19–22, 28, 60], and temperature [1, 2, 4, 8, 15, 17, 19, 41, 48, 56, 59]. We have also some information about the effect of cross-links which is manifested when we consider the chemical relaxation caused by secretive attack of chemical reagents to cross-linking portions [9, 33–38, 42, 49, 51, 57, 61]. On the other hand, recent molecular theories of viscoelasticity by Rouse [52], Bueche [10],[1] and Nakada [44] have made a molecular interpretation of the wedge portion in the relaxation spectrum possible and have introduced a theoretical slope of $-\frac{1}{2}$ in that portion. Again, there has been another type of molecular theory of viscoelasticity by Green and Tobolsky [29], Scott and Stein [57], Furukawa [27], and Yamamoto [62], taking into consideration the rates of breaking and formation of cross-links in network structure of high-polymeric substances. The latter-type molecu-

[1] The Bueche molecular theory has passed on a rather different mathematical approach from the others and has attained a similar result, while Ferry [20] has extended the Rouse theory on the dilute polymer solution to concentrated solutions and undiluted solids of linear polymers and has also obtained a theoretical slope of $-\frac{1}{2}$ in a skirt portion of the wedge.

lar theory may be available for molecular interpretation of the plateau region in the relaxation spectrum of rubberlike materials, of which concrete development has not been performed, while the former type's has been available for explaining the wedge portion in terms of intrachain relaxation mechanism, that is to say, a segment motion.

But for crystalline polymers as well as for textile fibers, of which the presence of crystal regions and the orientation of molecular chains are characteristic, there has been little information about the effects of these structural features, among other factors, on their relaxation spectra, except for some information about singular temperature resistibility of dynamic properties [7, 45, 55].

In the present paper, it is intended to demonstrate the effects of crystallization and molecular orientation upon the relaxation spectra of several typical fiber-forming polymers over rather wide range, using some physical treatments, such as heat treatment and cold-drawing.

The results of this investigation may be of use not only in their fundamental significance that they provide information about the effects of crystallization and molecular orientation upon the relaxation spectrum, but also in their applicability to textile industry, because they show what change of viscoelastic behavior occurs when glasslike amorphous polymers or crystalline ones are modified to textile fibers by means of such physical treatments as cold-drawing and heat treatment, familiar treatments for manufacturing synthetic fibers.

Apparatus and Procedure

The apparatus and method employed in this study were quite the same as those described in the previous paper [24]. Three different types of apparatus were used to make the following four kinds of dynamic measurement possible; namely, free damping vibration method for a subsonic range, forced vibration method for a lower audio range, and two acoustic methods, i.e., longitudinal wave resonance and propagation methods, for higher audio and supersonic ranges. The frequency range covered in this way was from 2×10^{-1} to 2×10^{5} c.p.s.

The sample was, in all cases studied, prepared in the form of filament, and the vibrational strain was limited to pure longitudinal mode only. An adequate static tension from 0.1 to 0.2 g./den. had to be applied on the sample strip during the particular experiment. The dynamic strain was always kept smaller than 0.1% to avoid the nonlinear effect and thus to ensure the validity of Boltzmann's superposition principle. During each experiment the air condition was kept at 23° C. and 65% R.H., and all sample strips were preconditioned for several days at this air condition. Sometimes, however, the strip was predried over phosphoric acid anhydrous or was preconditioned at other air condition for particular experimental purposes. Experimental results were represented in terms of the complex dynamic modulus as a function of applied frequency, and the relaxation spectrum was evaluated mainly from the imaginary part of the complex dynamic modulus using the so-called zeroth approximation method.

Four fiber-forming synthetic polymers, polyethylene terephthalate, polycaproamide, polyvinyl chloride and polyvinyl alcohol, were employed in this study on account of their respective characteristics in chain stiffness, chain interaction, and crystallinity.

The modifications of molecular orientation and crystallization of the sample strip were performed by cold-drawing up to maximum degree and by adequate heat treatment, as mentioned concretely in the following sections, and its degrees of molecular orientation and crystallization were evaluated from the measurements of double refractive index by means of the Berek compensator method and of density by the floating method, being supplemented by the X-ray diffraction pattern obtained by the ordinary Debye method using monochromatic parallel ray of CuK_{α}.

Experimental Results

1. *Polyethylene Terephthalate*

Polyethylene terephthalate (PET) is one of the characteristic fiber-forming crystalline polymers, of which weak chain interaction and high chain stiffness are characteristic. It is a favorable material for our experimental purposes, as will be recognized from the earlier X-ray studies by Astbury *et al.* [3] and by Hardy *et al.* [30]. Namely, the quenched polymer is an almost noncrystalline and nonoriented glasslike material, showing an X-ray diffraction pattern having a broad diffuse halo only, and is easily converted to either a crystalline and nonoriented or a highly oriented and crystalline polymer by either such a physical treatment as heat treatment or cold-drawing, respectively.

A polymer of PET having an intrinsic viscosity of 0.47 in 60:40 wt, % phenol/tetrachloroethane was converted to a continuous filament yarn of about 300 den. (30 fils) by means of an ordinary melt-spinning method followed by a quenching under as small a tension as possible. The filament thus prepared was modified to samples, as listed in Table I.

The results obtained were as follows:

1. *Effect of drawing.* The quenched filament, TR-0-0, was drawn by several degrees up to 400% at an ordinary commercial rate at 85° C., somewhat higher than the second-order transition temperature of this polymer.

The facts that the X-ray pattern is only a diffuse halo, as illustrated in Figure 1a, its double refractive index is as small as 0.0019, and its density is 1.340 [2] indicate that the quenched filament is almost nonoriented and noncrystalline. Any noticeable change in X-ray diffraction pattern is hardly found until the degree of drawing attains 200%, except for slight maxima appearing along the equator. The diffuse halo pattern changes suddenly to a type similar to the fiber pattern, as shown in Figure 1b, when the degree of drawing exceeds 300%. The double refractive index also then increases suddenly from 0.0167 for 230% to 0.199 for 320%. These show that the material changes from a poorly oriented and noncrystalline to a highly oriented and crystalline one suddenly at a degree of drawing near 300%.

[2] Somewhat greater than the value of 1.334 assumed by Daubeny *et al.* [12] for the density of entirely amorphous regions.

The viscoelastic behavior is shown in Figure 2 in terms of the dynamic modulus functions together with the mechanical loss tangent, tan δ, and in Figure 3 in terms of the relaxation spectrum.

The dynamic modulus functions are hardly changed until the degree of drawing attains 200%, except for either some increase or slight decrease of the imaginary part of the complex dynamic modulus on either the lower or the higher frequency side. Remarkable increases are found to occur over the whole frequency range herein covered when the degree of drawing exceeds 300%.

The relaxation spectrum of the original quenched filament is of a shallow wedge type having a maximum intensity of about 1×10^9 dynes/cm.^{2} at a relaxation time of about 1×10^{-6} sec. and a minimum of about 1×10^8 dynes/cm.^{2} at a time of about 1 sec. With increasing degree of drawing up to 200%, the spectrum somewhat increases on the longer time side, slightly decreases on the shorter time side and becomes a more shallow one. For the degree of drawing higher than 300%, the spectrum goes up about ten times as high as that for the lower degrees of drawing, over the whole range of relaxation times covered.

It is interesting to note from these experimental results that the change of viscoelastic behavior of PET with drawing conforms exactly to the corresponding change of polymer structure from a poorly oriented and almost noncrystalline to a highly oriented and crystalline one.

The quenched filament was drawn by 400% at

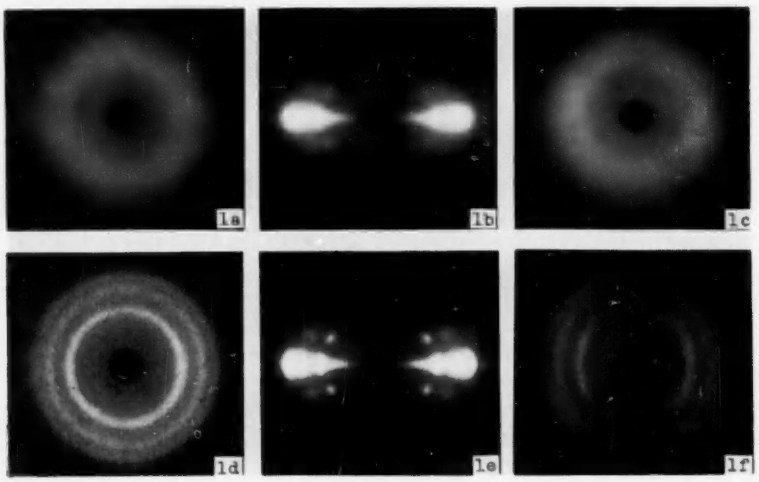


Fig. 1. The change of X-ray diffraction pattern of quenched and undrawn polyethylene terephthalate with treatments, where 1a, 1b, 1c, 1d, 1e and 1f correspond to TR-0-0, TR-85-5, TR-95-5, TR-0-0-H_2, TR-85-5-H_2 and TR-95-5-H_2, respectively.

75° and 95° C., using the same drawing speed as adopted above, to examine the effect of drawing temperature upon the various properties mentioned above.

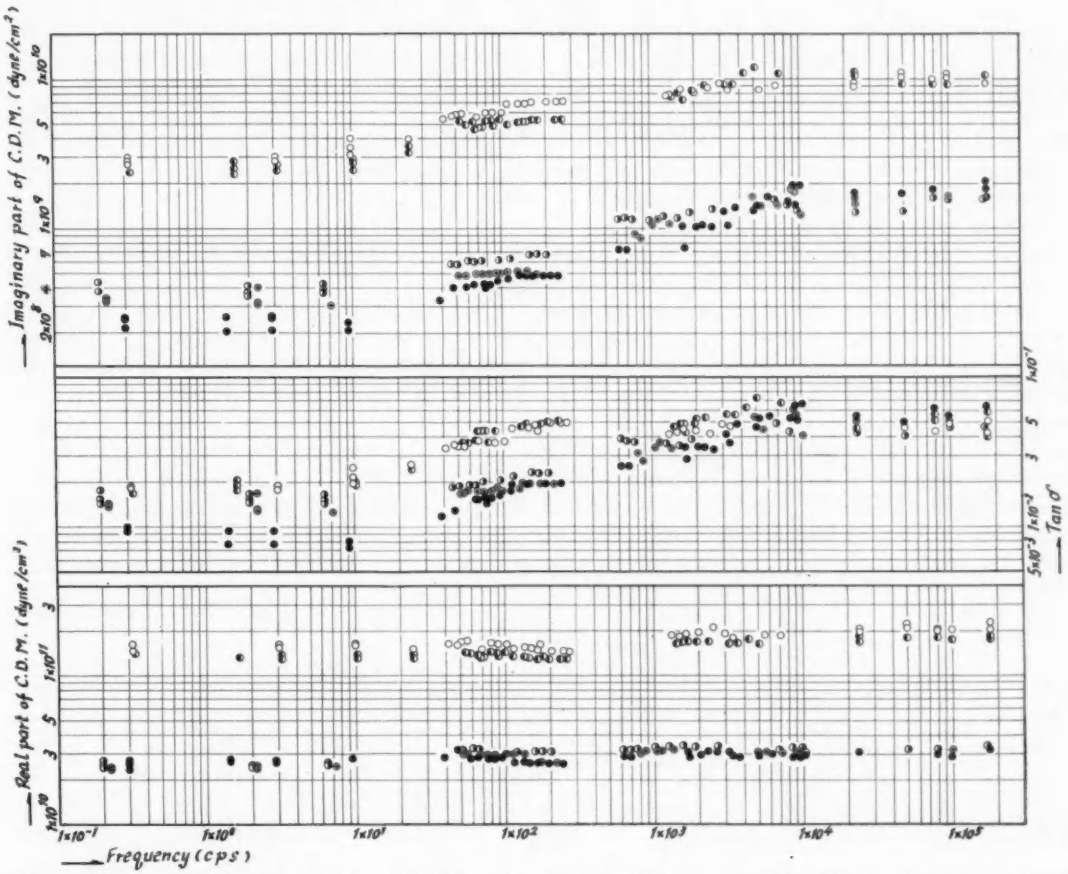


Fig. 2. The effect of drawing upon the complex dynamic modulus and the mechanical loss angle tangent of quenched and undrawn polyethylene terephthalate, where the marks ●, ◉, ◑, ◐ and ○ correspond to TR-0-0, TR-85-2, TR-85-3, TR-85-4 and TR-85-5, respectively.

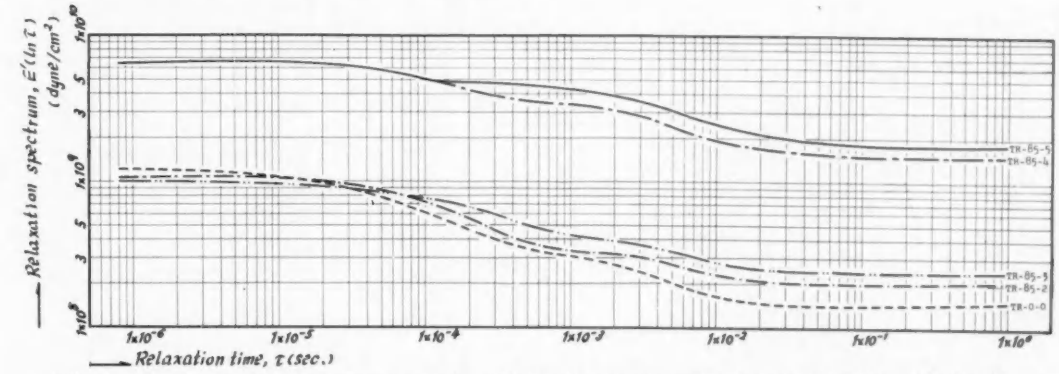


Fig. 3. The change of relaxation spectrum of quenched and undrawn polyethylene terephthalate with drawing.

The X-ray diffraction patterns were of a well-oriented fiber type for 75° C. and a diffuse halo for 95° C., and the corresponding double refractive indices were 0.219 and 0.0132, respectively. The viscoelastic behavior was quite similar to that of TR-85-5 and of TR-85-3, respectively. It is surprising that the increase of drawing temperature only by 10° C. maintains the structure poorly oriented and almost noncrystalline, and hampers occurrence of the remarkable change of viscoelastic behavior as mentioned before.

2. *Effect of heat treatment.* Both non- or poorly oriented and highly oriented filaments used above were heat-treated under constant length by respective degrees, as shown in Table I. The X-ray diffraction pattern, the density, and the double refractive index obtained for these heat-treated samples are given in Figure 1 and in Table I. It is observed from these data that the degree of crystallization of the filament increases more or less regularly, while the double refractive index changes somewhat in a complicated manner, as the progress of heat treatment. If we assume simply that the density of amorphous regions in a partially crystalline PET is the same as that assumed by Daubeny *et al.* [12], i.e., 1.334, for the completely amorphous PET and that the density of crystal regions in it is 1.455 according to their results from an X-ray study, it is concluded that the proportion by weight of crystal regions in the sample is increased from 5.4 to 45% for the nonoriented filament and from 25 to 45% for the highly oriented one, with progress of heat treatment.

On the other hand, the viscoelastic behavior, as shown in Figure 4 in terms of dynamic modulus functions, is hardly affected by the heat treatment, at least in the frequency range covered. Consequently, it may be considered that the viscoelastic behavior measured here is hardly influenced by the increase in degree of crystallization due to heat treatment.

2. *Polycaproamide*

Polycaproamide (PCA) is also a fiber-forming crystalline polymer suitable for demonstrating the influence of physical treatment, such as cold-draw-

TABLE I

Sample no.	Treatment	Density* (g./cc.)	Double refractive index† ($n_\gamma - n_\alpha$)	X-ray diffraction pattern
TR-0-0	Quenched and undrawn (original)	1.340	0.0019	A broad diffuse halo
TR-85-2	Drawn by 110% at 85° C.	—	0.0146	A broad diffuse halo
TR-85-3	Drawn by 230% at 85° C.	—	0.0167	A broad diffuse halo having slight maxima on the equator
TR-85-4	Drawn by 320% at 85° C.	—	0.199	Oriented and somewhat diffuse fiber pattern
TR-85-5	Drawn by 400% at 85° C.	1.362	0.232	Well-oriented and somewhat diffuse fiber pattern
TR-75-5	Drawn by 400% at 75° C.	—	0.219	Well-oriented and somewhat diffuse fiber pattern
TR-95-5	Drawn by 400% at 95° C.	—	0.0132	A broad diffuse halo
TR-0-0-H_1	Heat-treated at 120° C. for 1 hr.	1.377	0.0095	A system of defined rings
TR-0-0-H_2	Heat-treated at 150° C. for 10 min.	1.382	0.0040	A system of well-defined rings
TR-0-0-H_3	Heat-treated at 160° C. for 1 hr.	1.386	0.0040	A system of well-defined rings
TR-85-2-H_1	Heat-treated TR-85-2 at 120° C. for 1 hr.	—	0.0230	Poorly oriented and defined fiber pattern
TR-95-5-H_1	Heat-treated TR-95-5 at 120° C. for 1 hr.	—	0.0254	Poorly oriented and defined fiber pattern
TR-85-5-H_1	Heat-treated TR-85-5 at 120° C. for 1 hr.	1.377	0.256	Well-oriented and defined fiber pattern
TR-85-5-H_2	Heat-treated TR-85-5 at 150° C. for 10 min.	1.386	0.244	Well-oriented and defined fiber pattern

* Measured by floating method in benzene and carbon tetrachloride at 30° C.
† Measured by Bereck compensator under day-light at normal air condition.

ing and heat treatment, upon the viscoelastic behavior, and has the characteristics of strong chain interaction and of low chain stiffness in contrast to PET.

The quenched polymer is a pseudocrystalline and nonoriented material having an orthorhombic quasi-stable crystal system, which may be considered rather a state in the middle of an amorphous one, and is easily converted by either cold-drawing or heat treatment and aging to either a highly oriented or a nonoriented crystalline one having a monocrinic stable crystal system reformed by development of hydrogen bonded plane. The former system has been called an "α type" and the latter as "β type" by Okada et al. [47].

A polymer of PCA having intrinsic viscosity of 1.0 in m-cresol was converted to a monofilament of about 300 den. by an ordinary melt-spinning method followed by a quenching into ice water under as small a tension as possible.

The filament thus prepared was modified to the samples, NY-0-0 to NY-0-0-H, as listed in Table II.

The results obtained were as follows:

1. *The effects of drawing and heat treatment.* The quenched filament, NY-0-0, was drawn by several degrees up to 380% in warm water of 60° C., as shown in Table II. Samples NY-60-1 and NY-60-2 were drawn by hand as slowly as possible without necking, while the others were drawn at ordinary commercial rate.

The X-ray diffraction pattern of the quenched

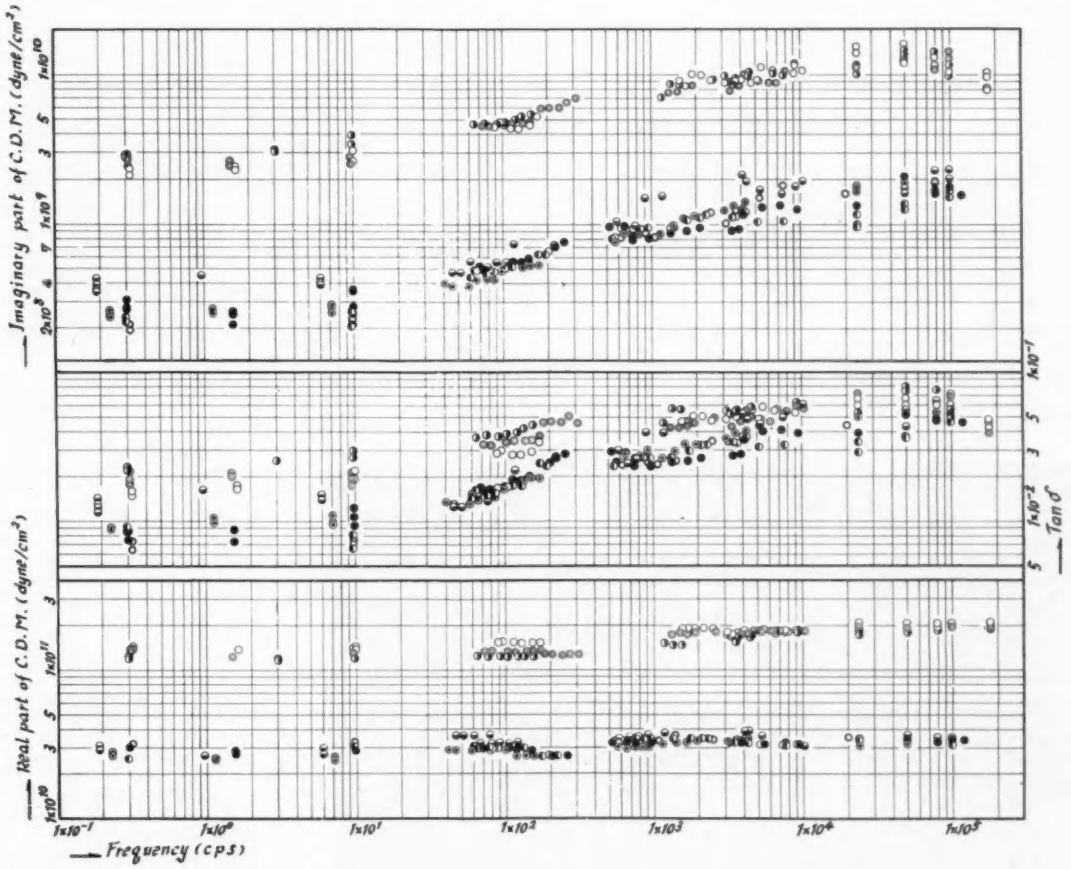


Fig. 4. The effect of heat treatment upon the complex dynamic modulus and the mechanical loss angle tangent of non- or poorly and highly oriented polyethylene terephthalates, where the marks ●, ◐, ○, ◉, ◒, ◎, ○ and ◑ correspond to TR-0-0-H_1, TR-0-0-H_2, TR-0-0-H_3, TR-85-2-H_1, TR-95-5-H_1, TR-75-5-H_1, TR-85-5-H_1 and TR-85-5-H_2, respectively.

filament is of a system of somewhat diffuse rings of almost α type, as illustrated in Figure 5a. The increase of drawing only by 30% almost changes the X-ray diffraction pattern of unoriented α type to a slightly oriented β type showing the appearance of stable hydrogen bonded planes, as in Figure 5b, where the density and the double refractive index also increase, as shown in Table II. Assuming simply that all of the crystal regions are β type, its density is 1.212 [47], and the density of entirely amorphous region is 1.100 [54a], the proportion by weight of crystal regions is estimated at about 29%. This may mean that the stable crystal region increases with slight increase in the degree of molecular orientation.

The change of the X-ray pattern in Figure 5 from *a* to *d* while increasing the degree of drawing up to 350% shows that the hydrogen-bonded plane in the crystal first becomes parallel to the fiber axis as found by Brill [6] and that the pattern successively

TABLE II

Sample no.	Treatment	Density* (g./cc.)	Double refractive index† ($n_\gamma - n_\alpha$)	X-ray diffraction pattern
NY-0-0	Quenched and undrawn (original)	1.127	0.0080	A system of some diffuse rings, almost α type
NY-60-1	Drawn by 30% at 60° C.	1.130	0.0093	Slightly oriented and some diffuse fiber pattern, $\beta \gg \alpha$
NY-60-2	Drawn by 100% at 60° C.	1.134	0.0290	Some oriented and somewhat diffuse fiber pattern, almost β type
NY-60-4	Drawn by 350% at 60° C.	1.140	0.0565	Well oriented and somewhat diffuse fiber pattern of β type
NY-60-5-B	Drawn by 380% at 60° C. and boiled in water for 1.5 hr.	1.143	0.0550	Well oriented and defined fiber pattern of β type, although the crystal orientation is somewhat relaxed
NY-60-5-BH	Heat-treated NY-60-5-B for 1 hr. at 130° C.	1.144	0.0610	Well oriented and defined fiber pattern of β type, although the crystal orientation is somewhat relaxed
NY-0-0-H	Heat-treated NY-0-0 for 10 min. at 170° C.	1.141	0.0133	Slightly oriented and defined fiber pattern, $\beta \gg \alpha$

* Measured by floating method in benzene and carbon tetrachloride at 30° C.
† Measured by Berek compensator under day-light at normal air condition.

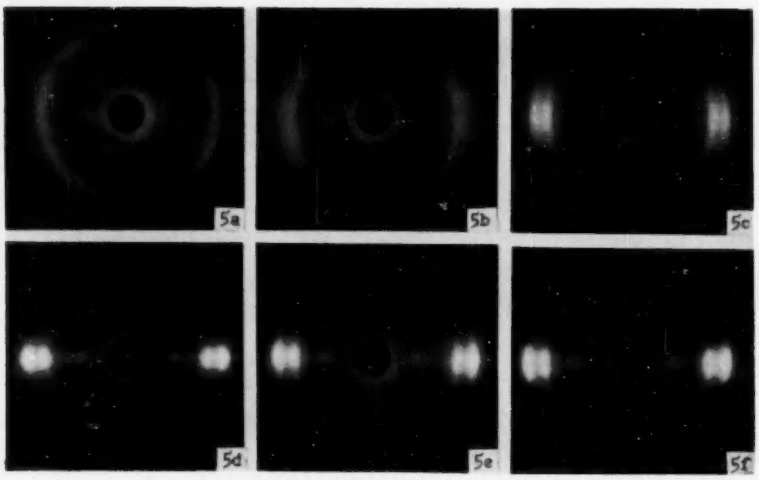


Fig. 5. The change of X-ray diffraction pattern of quenched and undrawn polycaproamide with treatments, where 5a, 5b, 5c, 5d, 5e and 5f correspond to NY-0-0, NY-60-1, NY-60-2, NY-60-4, NY-60-5-B and NY-60-5-BH, respectively.

becomes a well-oriented fiber type. The density and the double refractive index also increase successively. Thus, the proportion by weight of crystal regions seems to increase up to about 38% with increasing degree of molecular orientation.

The sample NY-60-5-B was drawn up to 380% and subsequently boiled in water for 1.5 hr. under constant length to extract the residual lactams, which otherwise act as a plasticizer [26], and the sample NY-60-5-BH was prepared by heating the former for 1 hr. at 130° C. under constant length. As recognized from the X-ray diffraction patterns, the crystal orientation is somewhat relaxed when compared with NY-60-4. The density increases regularly, while the double refractive index increases less regularly through a slight decrease for the former. Thus the proportion by weight of crystal regions increases up to about 42%, while the degree of molecular orientation seems to increase in a somewhat complicated manner.

Furthermore, the sample NY-0-0-H was prepared by heating the quenched filament under constant length for 10 min. at 170° C. Its X-ray diffraction pattern changes from α type to a distinctive β type and its density from 1.127 to 1.141. Thus, the proportion by weight of crystal region seems to increase up to about 39%.

The viscoelastic behavior is shown by the complex dynamic modulus function together with the mechanical loss tangent in Figure 6 and by the relaxation spectrum in Figure 7.

Comparing the results of quenched filament, NY-0-0, with those of 30% drawn one, NY-60-1, the real part of complex dynamic modulus somewhat decreases over the whole range covered, while the imaginary part also decreases on the lower frequency side and increases slightly on the higher frequency one. Thus, the relaxation spectrum somewhat decreases on the longer relaxation time side and slightly increases on the shorter time one. On

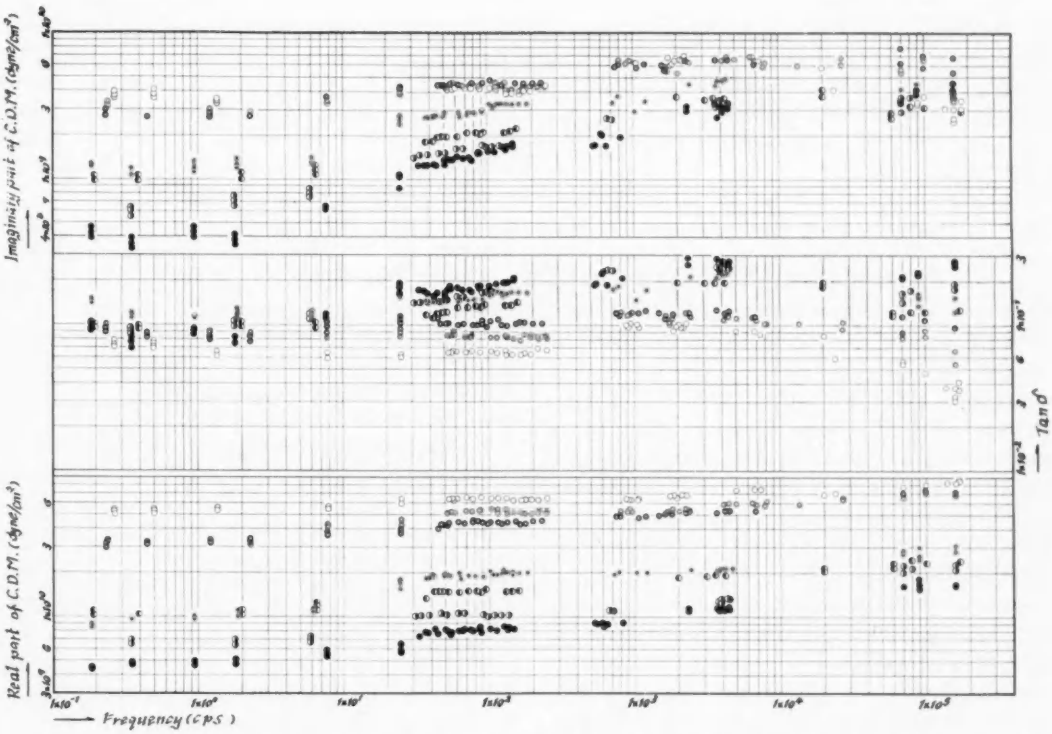


Fig. 6. The effects of drawing and heat treatment upon the complex dynamic modulus and the mechanical loss angle tangent of quenched and undrawn polycaproamide and the effects of boiling in water and of heat treatment upon those of highly drawn one, where the marks ◑, ●, ◉, ○, ◐, ◎ and ○ correspond to NY-0-0, NY-60-1, NY-60-2, NY-60-4, NY-0-0-H, NY-60-5-B and NY-60-5-BH, respectively.

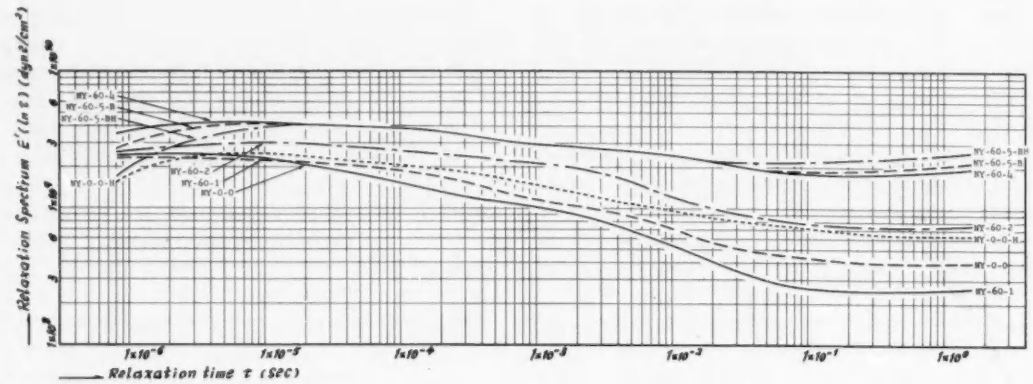


Fig. 7. The change of relaxation spectrum of quenched and undrawn polycaproamide with drawing and heat treatment and that of highly drawn one with boiling in water and heat treatment.

the other hand, for heat-treated filament, NY-0-0-H, the change of viscoelastic behavior is just in contrast to that obtained for NY-60-1.

When a limit of drawing near 30% is exceeded, the complex dynamic modulus successively increases with drawing over nearly the whole range covered, especially on the lower frequency side. Thus, the relaxation spectrum also increases mainly on the longer time side and changes from a shallow wedge to a box type.

The after treatments given to the drawn filaments somewhat increase the complex dynamic modulus mainly on the lower frequency side except for some decrease in the imaginary part of complex dynamic modulus on the higher frequency side, resulting in the corresponding changes on the spectrum, as shown in Figure 7.

In contrast to the case of PET, the effect of drawing upon the viscoelastic behavior seems to be limited mainly in the response on the lower frequency side, and the effect of heat treatment is somewhat distinctive, resulting in some increase and decrease in the relaxation spectrum on the longer and shorter relaxation time sides, respectively. Furthermore, the effect of drawing obtained at the first slight degree less than 30% is also singular.

2. *The effects of moisture contents.* To examine the effects of moisture content upon the viscoelastic behavior of such a hydrophillic polymer, the samples, NY-60-1, NY-60-5-B and NY-60-5-BH, were preconditioned at 23° C., 0 and 90% R.H. for several days and measured at the same air conditions to supplement the former measurement at 65% R.H. However, the air condition of 0% R.H. could not be maintained during observation on account of the lack of moisture insulation of the apparatus employed and was substituted by quick operation under about 40% R.H.[3]

Generally, the viscoelastic behaviors are noticeably affected by moisture contents; with decreasing moisture contents, the real part of complex dynamic modulus considerably increases over nearly the whole range covered, while the imaginary part increases on the lower frequency side and decreases, on the contrary, on the higher frequency one.

The corresponding relaxation spectrum is also affected noticeably by moisture contents, as illustrated in Figure 8; generally, with decreasing moisture contents, the spectrum increases on the longer relaxation time side and decreases on the shorter time one; and the effects are especially noticeable when the sample is extremely dried and are depressed with progress of the physical treatments.

It is noticeable that the effect of decreasing moisture content upon the viscoelastic behavior is very analogous to that of heat treatment.

The effect of average molecular weight upon the viscoelastic behavior was also examined for the quenched filaments having intrinsic viscosities of 0.47 and 0.68 in m-cresol. It was conclusive that the effect of average molecular weight is not marked, but the effect of aging is rather marked.

[3] The moisture content at the measurement was about 0.5%, which corresponds to the moisture regain at about 5% R.H.

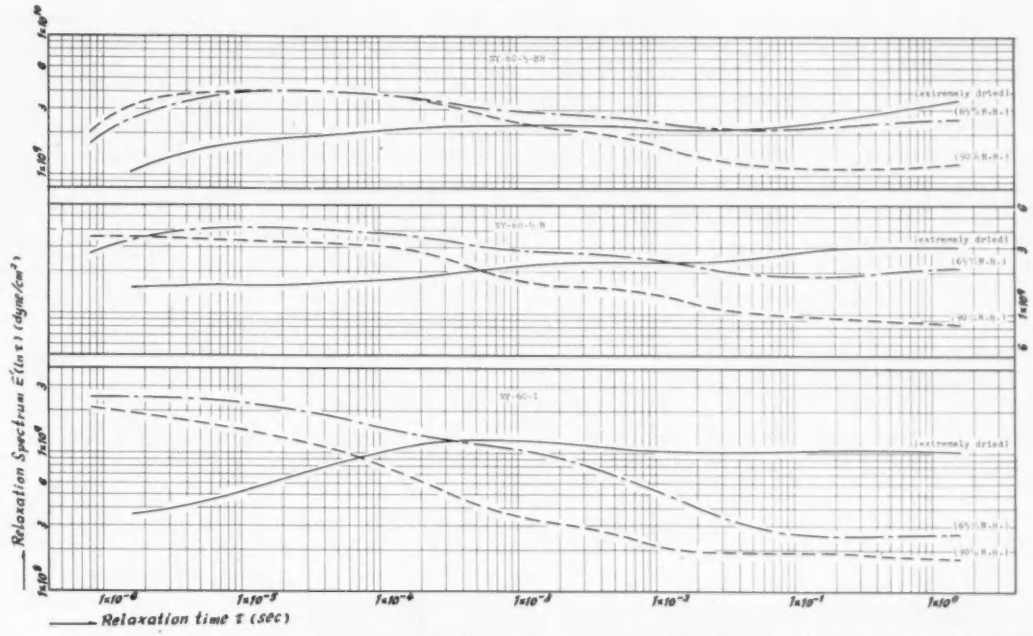


Fig. 8. The change of relaxation spectra of quenched, highly drawn, and highly drawn and heat-treated polycaproamides with moisture content.

TABLE III

Sample no.	Treatment	Density* (g./cc.)	Double refractive index† ($n_\gamma - n_\alpha$)	X-ray diffraction pattern
PVCl-0-0	Undrawn (original)	1.378	6.7×10^{-5}	Broad diffuse halo
PVCl-100-2	Drawn by 100% at 100° C.	1.386	2.2×10^{-4}	Broad diffuse halo
PVCl-100-3	Drawn by 200% at 100° C.	1.389	5.1×10^{-4}	Broad diffuse halo having slight maxima on the equator
PVCl-100-4	Drawn by 300% at 100° C.	1.391	2.5×10^{-3}	Few diffuse spots
PVCl-100-5	Drawn by 400% at 100° C.	1.391	2.7×10^{-3}	Few diffuse spots
PVCl-100-6	Drawn by 500% at 100° C.	1.392	2.8×10^{-3}	Few diffuse spots

* Measured by floating method in *n*-heptane and carbon tetrachloride at 30° C.
† Measured by Berek compensator under day-light at normal air condition.

3. *Polyvinyl Chloride*

In the former experiments, the polymers employed are all crystalline and the effect of molecular orientation due to drawing can not be well separated from the associating effect of crystallization.

In this experiment, therefore, polyvinyl chloride (PVCl), noncrystalline fiber-forming polymer of moderate chain interaction and low chain stiffness, is employed to demonstrate the effect of molecular orientation upon viscoelastic behavior alone.

The polymer, the average degree of polymerization $\bar{P}_v$, which is estimated at about 1400, was converted to a continuous filament yarn of about 1000 den. (50 fils) by the ordinary dry-spinning method extruding about 25% solution in 60 : 40 vol. % benzene/acetone under as small a tension as possible. Undrawn filament thus prepared was drawn at 100° C. by respective degrees up to 500%, as shown in Table III, by keeping the take-up rate constant, 70 cm./min., and varying the let-off one.

The X-ray diffraction patterns of the filaments

thus prepared are almost amorphous ones, as shown in Figure 9, changing from a broad diffuse halo to a very few diffuse spots with progress of drawing. The double refractive index, the values of which are extremely small in comparison with those of other polymers, increases successively with drawing and attains a value of about 3×10^{-3} as shown in Table III, and the density also increases as likely as the double refractive index.

The facts show qualitatively that the molecular orientation is improved successively with drawing and attains a maximum degree, while the crystallization hardly arises.

The viscoelastic behavior is shown in Figure 10 in terms of the complex dynamic modulus function together with the mechanical loss tangent and in Figure 11 in terms of the relaxation spectrum, respectively.

The real and the imaginary parts of complex dynamic modulus increase successively with drawing over the whole frequency range herein covered and seem to attain maximum values. Thus, the relaxation spectrum also increases nearly uniformly over the whole range herein covered, as shown in the figure. The fact that the spectrum increases with drawing in such a uniform way as just mentioned seems to be in common with that for polyethylene terephthalate.

In this case, the effect of crystallization is negligible and thus the change of viscoelastic behavior due to drawing may be ascribed mainly to that of the degree of molecular orientation itself.

4. *Polyvinyl Alcohol*

Polyvinyl alcohol (PVA) is a crystalline polymer, of which chain interaction is strong, chain stiffness is low and spacial symmetry of chain seems to be somewhat poor, and it is also a suitable polymer to demonstrate the influence of the physical treatments, especially that of heat treatment, upon the visco-

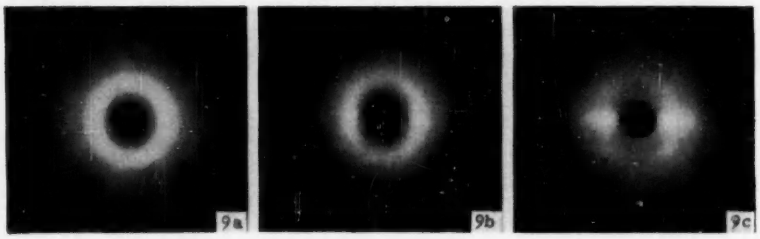


Fig. 9. The change of X-ray diffraction pattern of undrawn polyvinyl chloride with drawing, where 9a, 9b and 9c correspond to PVC1-0-0, PVC1-100-3 and PVC1-100-6, respectively.

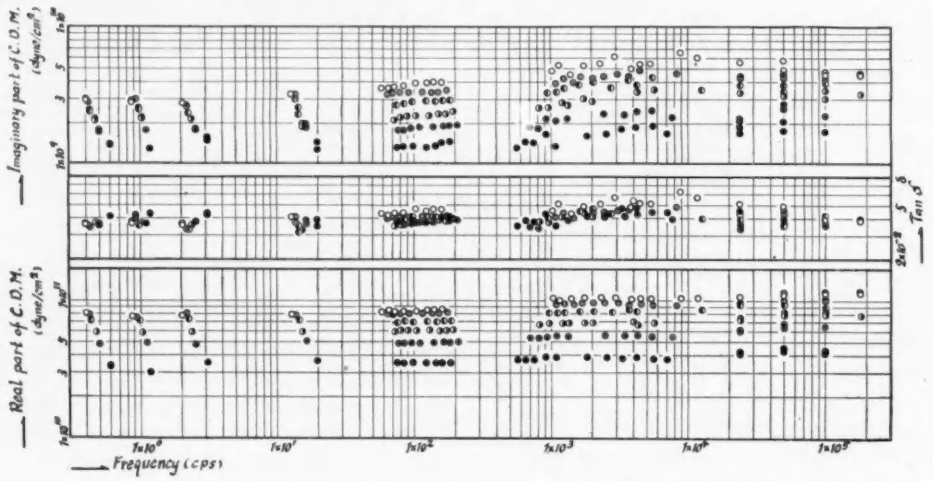


Fig. 10. The effect of drawing upon the complex dynamic modulus and the mechanical loss angle tangent of undrawn polyvinyl chloride, where the marks ●, ◉, ◑, ◐, ◎ and ○ correspond to PVC1-0-0, PVC1-100-2, PVC1-100-3, PVC1-100-4, PVC1-100-5 and PVC1-100-6, respectively.

elastic behavior, as will be recognized from such a simple fact that the polymer non-heat-treated is easily dissolved by warm water, while heat-treated one is not already dissolved even in boiling water, being reinforced by the development of crystal regions.

The polymer used was prepared by more than 99% hydrolysis of polyvinyl acetate, and its average degree of polymerization, $\bar{P}_n$, was estimated at about 1600.

The polymer was converted to a continuous monofilament of about 300 den. by extruding about 50% aqueous solution at about 90°C. The filament thus prepared was air-dried for several days and subsequently modified to the samples, as listed in Table IV.

The results obtained were as follows:

1. *The effect of drawing.* The original filament, PVA-0-0, was drawn by several degrees up to 220% at 90° C., as shown in Table IV, by keeping the take-

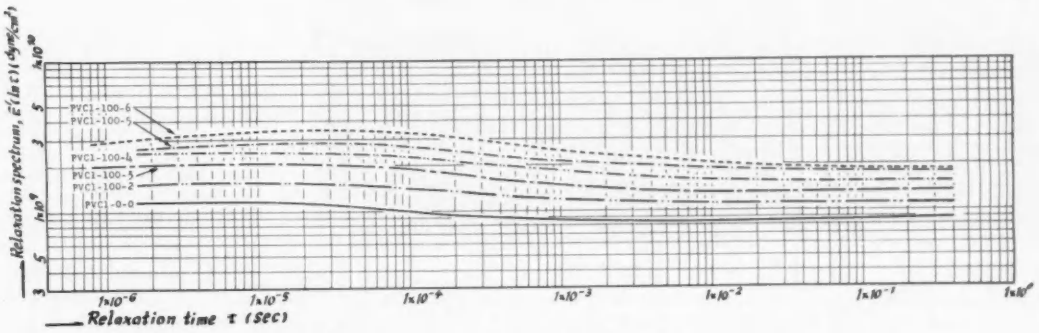


Fig. 11. The change of relaxation spectrum of undrawn polyvinyl chloride with drawing.

TABLE IV

Sample no.	Treatment	Density* (g./cc.)	Double refractive index† ($n_\gamma - n_\alpha$)	X-ray diffraction pattern
PVA-0-0	Undrawn (original)	1.284	0.0009	System of somewhat diffuse rings
PVA-90-1	Drawn by 30% at 90° C.	1.284	0.0059	Slightly oriented and somewhat diffuse fiber pattern
PVA-90-2	Drawn by 70% at 90° C.	1.286	0.0074	Somewhat oriented and somewhat diffuse fiber pattern
PVA-90-3	Drawn by 220% at 90° C.	1.287	0.0256	Well oriented and somewhat diffuse fiber pattern
PVA-0-0-H_1	Heat-treated at 120° C. for 10 min.	1.292	0.0018	System of rings
PVA-0-0-H_2	Heat-treated at 160° C. for 10 min.	1.293	0.0043	System of defined rings
PVA-0-0-H_3	Heat-treated at 210° C. for 10 min.	1.306	0.0052	System of well defined rings
PVA-90-3-H_4	Heat-treated PVA-90-3 at 230° C. for 10 min.	1 303	0.0295	Well oriented and defined fiber pattern
PVA-0-0-B_1	Dipped freely in 0.5% aqueous solution of boric acid for a week at 15° C.	1.295	—	—
PVA-0-0-B_2	Dipped freely in 1.0% aqueous solution of boric acid for a week at 15° C.	1.297	—	—
PVA-0-0-B_3	Dipped freely in 5.0% aqueous solution of boric acid for a week at 15° C.	1.319	—	System of a diffuse ring

* Measured by floating method in benzene and carbon tetrachloride at 30° C.
† Measured by Berek compensator under day-light at normal air condition.

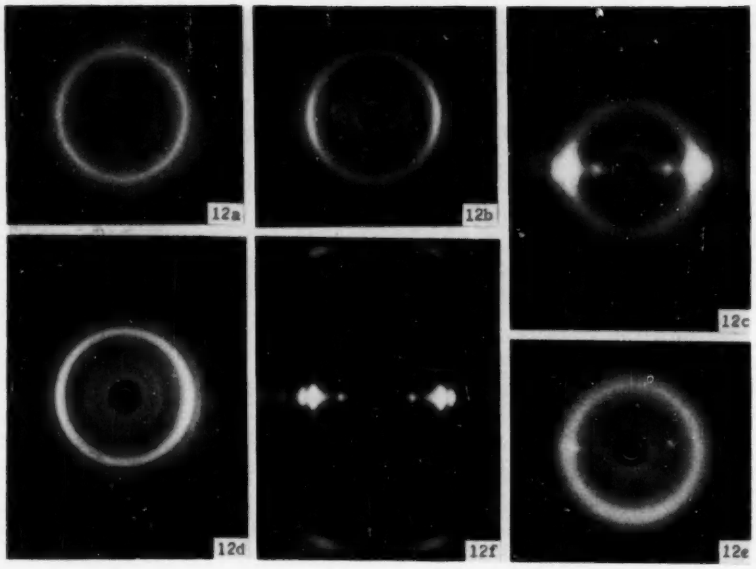


Fig. 12. The change of X-ray diffraction pattern of undrawn polyvinyl alcohol with treatments, where 12a, 12b, 12c, 12d, 12e and 12f correspond to PVA-0-0, PVA-90-2, PVA-30-3, PVA-0-0-H_8, PVA-0-0-B_8 and PVA-90-3-H_4, respectively.

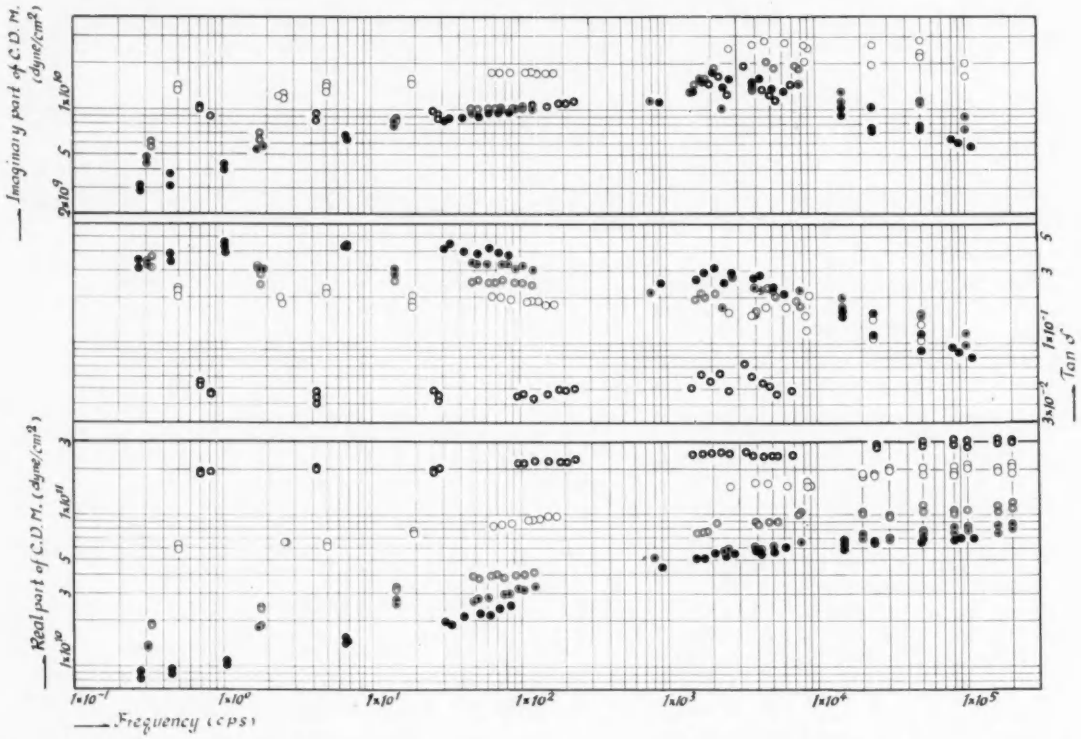


Fig. 13. The effect of drawing upon the complex dynamic modulus and the mechanical loss angle tangent of undrawn polyvinyl alcohol and the effect of heat treatment upon those of highly drawn one, where the marks ●, ◉, ◎, ○ and ⭘ correspond to PVA-0-0, PVA-90-1, PVA-90-2, PVA-90-3 and PVA-90-3-H_4, respectively.

up rate constant, 200 cm./min., and varying the let-off one.

The X-ray diffraction pattern changes, as shown in Figure 12a to 12c, from a system of somewhat diffuse rings to a somewhat diffuse fiber pattern and the double refractive index successively decreases from 0.009 to 0.0256. The density does not increase so much as in the former. It shows that the molecular orientation is successively improved, especially in the range of drawing higher than 70%, while the degree of crystallization is slightly improved, being retained at about 23 to 27%.[4]

The viscoelastic behavior is shown in Figure 13 in terms of the dynamic modulus function together with the mechanical loss tangent, and in the upper part of Figure 14 in terms of the relaxation spectrum.

With increasing degree of drawing, the real part of complex dynamic modulus increases over the whole frequency range herein covered, in which the increase is rather obvious on the lower frequency side, while the imaginary part increases on both frequency sides until the degree of drawing attains 70%, and goes up over nearly the whole frequency range when the limit of drawing, 70%, is covered.

The relaxation spectrum of the original filament is represented by a broad distribution, having a maximum intensity of about 1×10^{10} dyne/cm.^{2} at a relaxation time of near 1×10^{-4} sec. With increasing degree of drawing up to 70%, the spectrum increases on both the time sides and becomes a broader one. For the degree of drawing higher than 70%, the spectrum increases over the whole range covered, in which the increase is also somewhat obvious on the longer relaxation time side.

The fact that the increase with drawing in the real part of the complex dynamic modulus at the lowest frequency measured is far larger than that in the imaginary part in the frequency range covered herein, suggests that the greater increase in the relaxation spectrum should be expected at a somewhat longer relaxation time than that covered herein.

[4] The value, the proportion by weight of crystal region, was estimated, assuming that the density of crystal region is 1.345 and that of entirely amorphous one 1.267 [53].

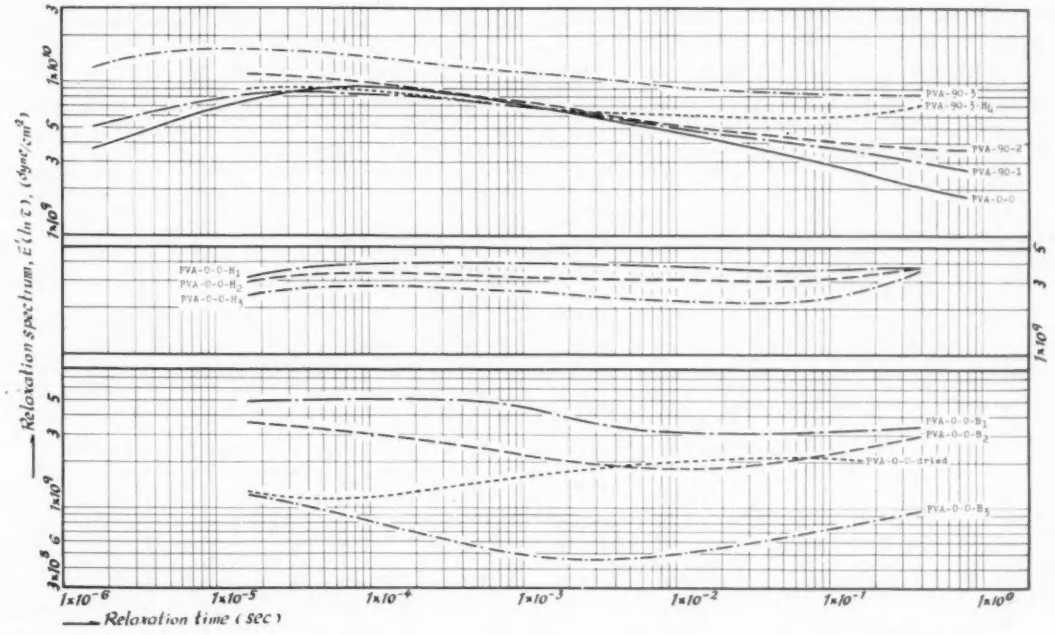


Fig. 14. Upper part; the change of relaxation spectrum of undrawn polyvinyl alcohol with drawing and that of highly drawn one with heat treatment.

Middle part; the change of relaxation spectrum of undrawn polyvinyl alcohol with heat treatment.

Lower part; the change of relaxation spectrum of undrawn polyvinyl alcohol with chemical treatment, using boric acid, and with drying.

The effect of drawing upon the viscoelastic behavior is not similar to the case of PET, but is rather similar to the case of PCA in the sense that the effect is more obvious in the lower frequency response.

2. *The effect of heat treatment.* Both non- and highly drawn filaments used above were heat-treated by respective degree, as shown in Table IV, by keeping the length constant. The changes of X-ray diffraction pattern, density, and double refractive index are shown in Figure 12 and Table IV. It is observed from these data that the degree of crystallization is increased regularly, while the molecular orientation is slightly improved. According to the simple estimation of the degree of crystallization from the density measured, it is concluded that the proportion by weight of crystal region in the sample is increased from 23 to 52% for undrawn filament and from 27 to 48% for highly drawn one, respectively.

The viscoelastic behavior, as shown in Figure 13 for highly drawn filament and in Figure 15 for undrawn one, both in terms of dynamic modulus function, and in Figure 14 for both in terms of relaxation spectrum, changes remarkably with progress of the treatment; for both the filaments, the real part of complex dynamic modulus increases in order with progress of the treatment, the increase of which is more obvious on the lower frequency side, while the imaginary part decreases mainly on the higher frequency side and increases on the lower frequency side, regularly also. The facts not only show that the relaxation spectrum in the time range covered herein decreases regularly with progress of the treatment, as shown in Figure 14, but also suggest that the spectrum at longer relaxation time than that covered herein may also increase regularly with progress of the treatment.

It may be concluded that the effect of heat treatment is similar to the case of PCA and is rather remarkable.

3. *The effects of moisture content and a chemical treatment, using boric acid.* Furthermore, in order to supplement the effect of heat treatment, the effects of moisture content, and a chemical treatment, dipping the filament in aqueous solution of boric acid, were examined.

For the former experiment, the original filament,

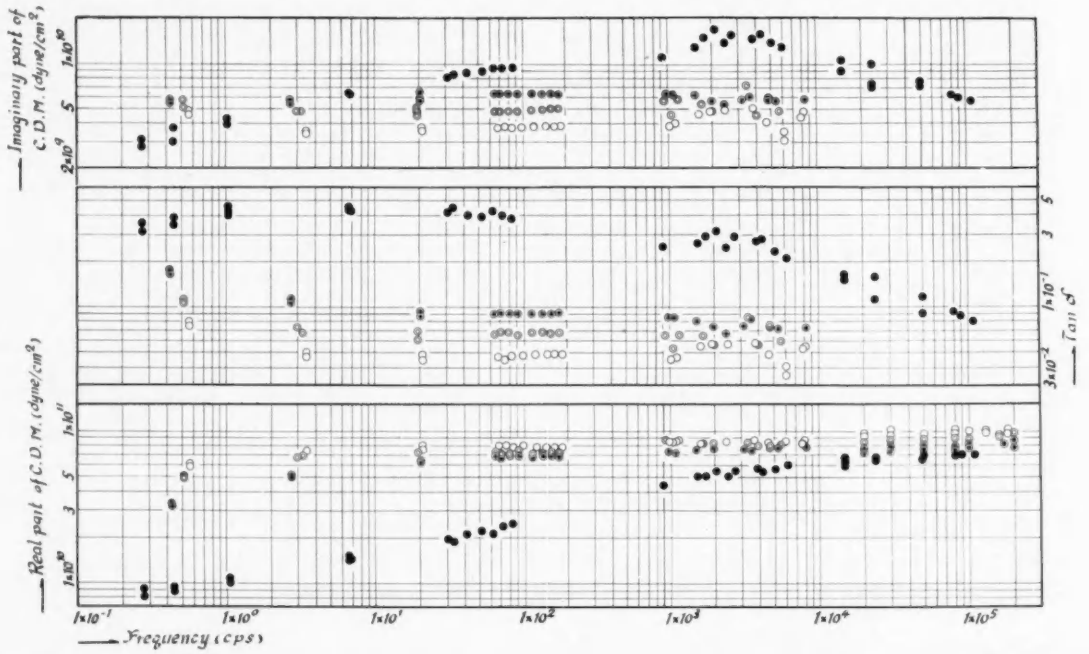
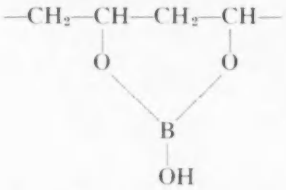


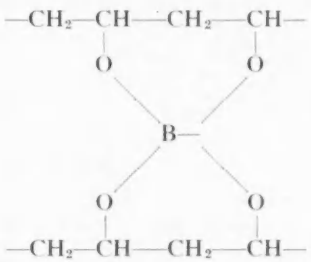
Fig. 15. The effect of heat-treatment upon the complex dynamic modulus and the mechanical loss angle tangent of undrawn polyvinyl alcohol, where the marks ●, ◉, ◎ and ○ correspond to PVA-0-0, PVA-0-0-H_1, PVA-0-0-H_2 and PVA-0-0-H_3, respectively.

PVA-0-0, was preconditioned at 23° C., 0% R.H. for several days, and was measured by quick operation at 23° C., about 40% R.H.[5] While for the latter experiment, the original filament was modified to the samples from PVA-0-0-B_1 to PVA-0-0-B_3, dipped freely in aqueous solutions of boric acid, as shown in Table IV, and air-dried subsequently.

It is well known that boric acid as well as borax reacts with polysaccarides and other polyoxy compounds and yields molecular compounds. According to Deuel et al. [13], boric acid reacts with aqueous solution of polyvinyl alcohol and yields a monodiol complex as follows:



On the other hand, according to the X-ray study by Sakurada et al. [54], it has been assumed that the reaction of boric acid with polyvinyl alcohol swollen by water yields the monodiol complex as mentioned above, and the complex changes with drying to a didiol complex as follows.



Furthermore, it has been suggested also that the crystal region is destroyed regularly with progress of the treatment, as shown briefly in Figure 12e for PVA-0-0-B_3, in addition to the modification of the crystal system as mentioned above; the material at dry state is changed regularly from crystalline to cross-linked amorphous one in the sense that the neighboring molecular chains in the amorphous region are also cross-linked with each other in such a way, forming the didiol complex, as mentioned above.

For both the dried sample and the treated ones, the viscoelastic behavior is shown in Figure 16 in terms of the dynamic modulus and in the lower part of Figure 14 in terms of the relaxation spectrum. It is observed that the effects of decreasing moisture content and the chemical treatment upon the viscoelastic behavior are very marked and that the effects are similar not only to each other but also to that of the heat treatment, showing considerable decrease of the relaxation spectrum in the relaxation time range herein covered and presumable increase in the spectrum at somewhat longer relaxation time than that herein covered, except some difference between respective effects in every detail. It may be noted that the effect of the chemical treatment upon the viscoelastic behavior is similar to that of the heat treatment in spite of inverse effects of the treatments upon the degree of crystallization; by the chemical treatment the crystal region is destroyed, but by the heat treatment the region is rather developed.

[5] The moisture content at the measurement was about 2%, which corresponds to the moisture regain at about 15% R.H.

Discussion and Conclusion

Summarizing the effects of drawing upon the viscoelastic behavior, we can classify the effects as follows: for PET and PVCl, the relaxation spectrum increases with drawing almost uniformly over the relaxation time range herein covered, while for PVA and PCA, the increase of the spectrum is obviously on the longer relaxation time side. The singularity seems to correlate with the nature of the polymer employed; namely, the stronger the chain interaction besides the hydrophillicity of the polymer, the more obvious the singularity may be.

On the other hand, summarizing the effects of heat treatment upon the viscoelastic behavior, we can also classify the effects as follows; for PET, the relaxation spectrum is hardly affected by the treatment in spite of the greater development of crystallization, while for PCA and PVA, the spectrum is decreased on the shorter relaxation time side and is increased on the longer relaxation time side with progress of the treatment. The singularity also seems to correlate with the nature of the polymer employed, not with the crystallinity but with the chain interaction in addition to the hygroscopicity of the polymer, as mentioned above.

As a matter of practice, the improvement of molecular orientation due to drawing is attended by the development of crystallization as well as that of lateral bonding between chain molecules in the

amorphous region, while the development of crystallization due to heat treatment is also attended by that of the lateral bonding, so long as ordinary crystalline polymers of good spacial symmetry and of strong chain interaction are employed. Thus, the effects of drawing or of heat treatment upon the viscoelastic behavior can be strictly ascribed to neither the improvement of molecular orientation, the development of crystallization nor that of lateral bonding between the chains in the amorphous region, separately.

However, the effects of heat treatment upon the viscoelastic behavior should not be ascribed to the development of crystallization, but rather to that of lateral bonding between the chains in the amorphous region. The concept is strongly supported not only by the information about the effect of heat treatment upon the viscoelastic behavior of undrawn and highly drawn PETs, in which the viscoelastic behavior is hardly affected by the increase in the degree of crystallization so long as the degree of molecular orientation is kept constant. It is supported also by the facts that the effect of decreasing moisture content is analogous with that of heat treatment upon the viscoelastic behavior of such hydrophillic polymers as PVA and PCA and that the effect of chemical treatment, using boric acid, is also analogous with that of heat treatment upon the viscoelastic behavior of PVA, in spite of quite inverse effects of the treatments upon the degree of crystallization.

Indeed, the effect of decreasing moisture content upon the viscoelastic behavior of such a hydrophillic polymer as either PCA or PVA should be ascribed to decreasing chain mobility in the amorphous region due to decreasing free water, which otherwise

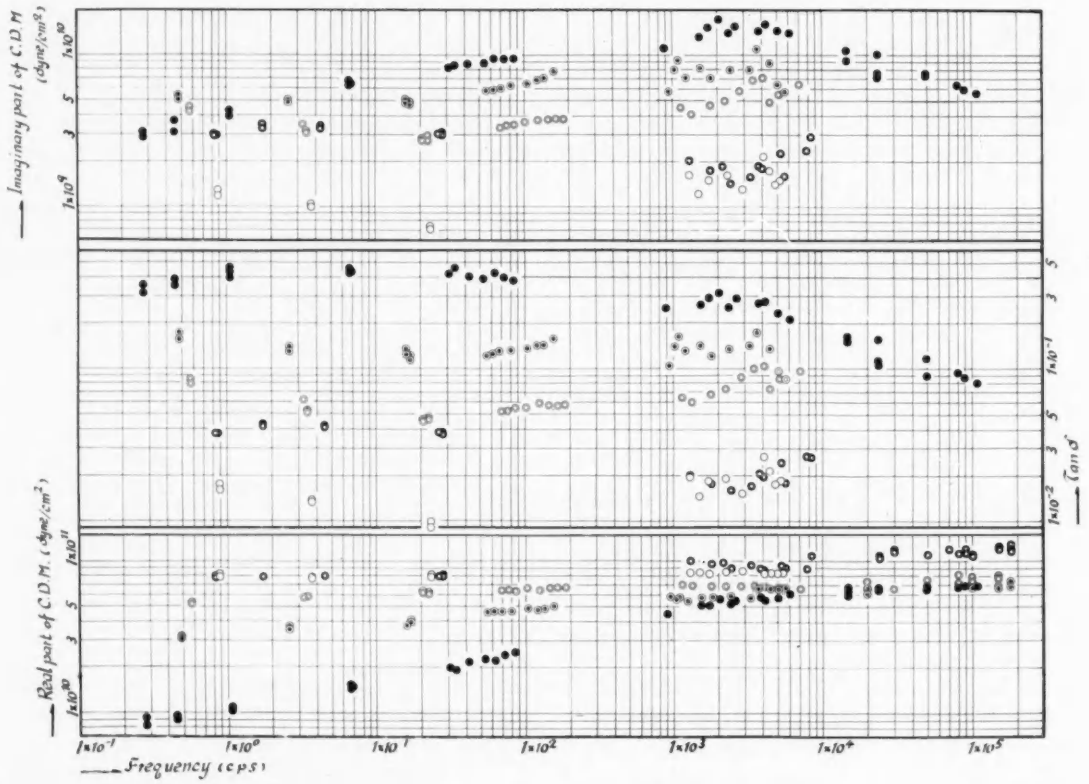


Fig. 16. The effects of chemical treatment, using boric acid, and of drying upon the complex dynamic modulus and the mechanical loss angle tangent of undrawn polyvinyl alcohol, where the marks ●, ◉, ◎, ○ and ◎ correspond to PVA-0-0, PVA-0-0-B_1, PVA-0-0-B_2, PVA-0-0-B_3 and PVA-0-0 dried, respectively.

acts as a plasticizer, and to dehydration of either CO and NH groups [6] or OH groups and development of hydrogen bridge between them, and is never ascribed to anything dealing with the crystal region; since, for example, it has been well known from the X-ray study of PVA [53] that the crystal region is hardly destroyed by water even in swollen state at room temperature. The effect of the chemical treatment, using boric acid, upon the viscoelastic behavior of PVA is also ascribed to decreasing chain mobility in the amorphous region due to development of boron bridge and may not be ascribed to anything concerned with the crystal region.

Again, the effect of drawing upon the viscoelastic behavior should not be ascribed to the development of crystallization accompanied with the improvement of molecular orientation, but rather to the improvement of molecular orientation itself in the amorphous region. The concept is not only supported by general information about the effect of crystallization due to heat treatment mentioned above, but also supplemented by the results obtained for drawing PVCl, in which the crystallization hardly arises.

In such concepts as mentioned above, some singular effects upon the viscoelastic behavior obtained for drawing such hydrophillic polymers of strong chain interaction as PCA and PVA may be interpreted in terms of superposing the effect of improving molecular orientation upon that of associated development of lateral bonding between the chains in the amorphous region. Furthermore, the inverse effect upon the viscoelastic behavior obtained for drawing PCA at the first slight degree may also be interpreted not by slight improvement of molecular orientation but by destruction of some quasi-stable lateral bonding between the chains in the amorphous region, which otherwise decreases the chain mobility.

Consequently, it can be tentatively concluded that the viscoelastic response of typical crystalline polymers, such as polyethylene terephthalate, polycaproamide and polyvinyl alcohol, in the range of frequencies from subsonic to supersonic, is hardly correlated with the presence of crystal region but is influenced rather markedly by the nature of the amorphous region manifested by chain interaction and chain stiffness as well as by chain orientation.

The relaxation spectrum is generally increased by increasing the degree of molecular orientation over the range of relaxation time herein covered. On the other hand, the relaxation spectrum is increased on the longer relaxation time side and is decreased on the shorter time side with decreasing chain mobility in the amorphous region; or it may be speculated that the relaxation spectrum is shifted to longer relaxation time side with decreasing chain mobility, although the shifting may not be done in such a way, keeping the whole form of spectrum constant, as expected for shifting the spectrum of the thermorheological simple material with changing temperature.

Again, it may be concluded that the relaxation spectrum of the crystalline polymers employed here is generally intensive not only over the range of relaxation times herein covered but also in the range of longer relaxation times than those covered here, and is not so essentially different from those obtained for such typical glasslike amorphous polymers as polyvinyl chloride [4], polystylene [4, 28], polyvinyl acetate [60], polyvinyl formal [25] and polymethylmetacrylate [4, 5] as from those for typical rubberlike materials, showing that either chain interaction or chain stiffness in such crystalline and glasslike amorphous polymers as mentioned above is too strong or too high to demonstrate either effect upon the relaxation spectrum in every detail over the range of relaxation times herein covered in comparison with those of rubberlike materials.

Any essential difference between the spectra of typical fiber-forming crystalline polymer and glasslike amorphous polymer can not be found in the relaxation time range herein covered. However, if there is some essential difference between them, it may be found on the relaxation spectrum at far longer relaxation times than those covered here, being manifested by the presence of a distribution of such interchain relaxation mechanisms of far longer relaxation times than those maintained by the crystal region.

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[6] The amount of hydrated groups was estimated by Hoshino et al. [31] as considerably small.

and to Dr. T. Kondo in our department for his kind help in measuring the double refractive index of the samples employed.

The authors are also indebted to Mr. Y. Sone of the Institute for Chemical Research for his kind help in preparing the PVA samples, to the Research Institutes of the Teikoku-Rayon Co., the Toyo-Rayon Co. and the Nihon-Rayon Co. for kindly furnishing the other samples employed, and to the Minister of Education of Japan for his financial support from 1953 to 1954.

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Chemical Damage in Wool

Part I: Determination by Paper Chromatography

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Abstract

A paper chromatographic method for determining the extent of damage by oxidizing or alkaline solutions to wool fabrics of unknown history is described. The presence of other textile fibers does not constitute an interference.

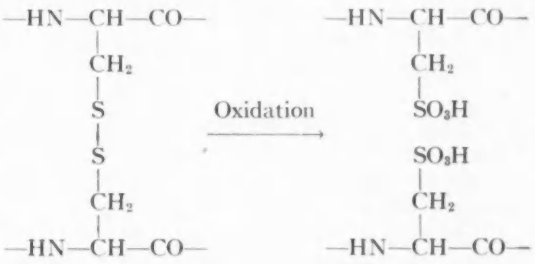
Introduction

Many methods have been proposed for the detection of damage in wool resulting from attack by oxidizing or alkaline solutions. Alkali solubility [15] the Allwörden reaction [4, 5], the K.M.V. reaction [17], acid solubility [28], and staining tests [19] are most often mentioned. Unfortunately, all of these methods have certain common disadvantages. The specificity of each is questionable, the history of the sample must be known precisely, and an undamaged sample of the same wool must be available. In some fabrics, e.g., papermakers' felts, degradation of the wool fiber may have occurred by reason of some previous treatment or exposure to damage and it becomes necessary to identify the damage in such fabrics having a completely unknown history. This study deals with a method developed to eliminate the above limitations.

Discussion

When wool fibers are exposed to oxidizing agents or alkali, definite chemical changes occur in the protein structure. These changes provide the most satisfactory evidence of the type and extent of chemical attack. The most sensitive point of wool protein is the disulfide cross-link of cystine. The rupture of this bond is responsible for most of the loss of tensile properties which occurs in wool fibers upon damage by oxidation or strong bases. This strength loss is largest in the wet fiber where hydrogen bonds are less effective.

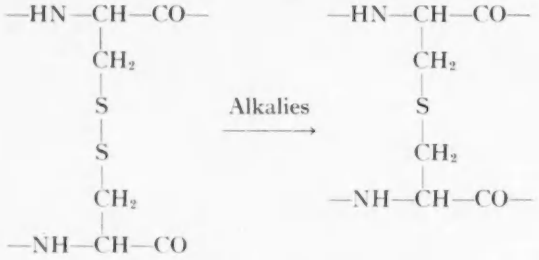
The reaction between wool and oxidizing agents has been studied at length by a number of investigators. Hydrogen peroxide [9, 22, 24], organic peracids [1, 8, 25], halogens [2, 3, 10, 12] and photochemical oxidation [10] all cause the formation of cysteic acid from cystine.



The amount of conversion is dependent on the particular oxidizing agent and on the conditions. In general, the quantity of cysteic acid formed is di-

rectly related to the degradation of the fiber. Since cysteic acid is formed in wool only by oxidation, its detection can be made the basis for a specific test for this type damage.

A number of reagents including alkaline solutions and cyanides bring about the conversion of combined



cystine in wool to lanthionine [11, 14, 16, 23, 27]. The mechanisms [6, 11, 18, 20, 21] by which lanthionine is produced differ both quantitatively and qualitatively since all the cystine can be converted to lanthionine by cyanide but only 50% by alkali. Thus it should be possible to develop a method which would differentiate between these two types of damage. In practice, however, alkali is the principal cause of cystine conversion to lanthionine.

To specifically test for oxidation and alkaline damage, it was necessary to develop a method which would determine the amino acid content of wool. Until the development of paper chromatography [7], the separation of the amino acids in a protein such as wool was a complex process. Consden, Gorden, and Martin [10] first used this technique to effect the separation of cysteic acid and lanthionine from wool hydrolysates. They examined both one- and two-dimensional chromatograms but did not develop a method which would separate both acids on the same sheet. Zahn [26, 27] describes both one- and two-dimensional chromatograms of the hydrolysates of chemically modified wool. Differentiation between spots was not as clear-cut as desired. Since in some fabrics, such as papermakers' felts, the cause of damage is unknown, it is most desirable that the presence of either amino acid should be detectable. Moreover, cystine should be discernible for comparative purposes.

Many solvent systems which failed to give the desired degree of separation were examined. Finally, by using solvents suggested by Hardy, Holland, and Nayler [13] lanthionine, cysteic acid, and cystine in wool hydrolysates were distinctly separated on a two-dimensional chromatogram. Of the other 15 amino acids present in the hydrolysate, only histidine and methionine were poorly visible. Therefore, other changes in the amino acid content of the wool are also readily detectable.

With experience or by the use of standards, the degree of damage may be gauged by the intensities of the spots of cystine and its degradation products. Conditions causing very small changes in the physical properties of the wool fiber are recognizable. The presence of other textile fibers does not constitute an interference although the sample size should be increased proportionately.

Experimental

Preparation of Sample

The sample should be reasonably free of foreign material. Percentages of cotton, nylon, Dacron, or other textile fibers do not interfere except that allowance should be made in the sample size.

The wool sample is hydrolyzed to its component amino acids by one of two different methods. In the first method, a sample containing 0.25 g. of wool is placed in a thick wall Pyrex test tube and 10 ml. of 6*N* hydrochloric acid is added. The tube is sealed and put into a stainless steel beaker or other metal container. After being heated in an oven at 125° C. for 5 hr., the tube is cooled and broken open. The dark-colored contents are filtered into an evaporating dish and evaporated to dryness on a steam bath. The residue is placed overnight in a desiccator containing potassium hydroxide pellets and then dissolved in 25 ml. of aqueous 10% isopropyl alcohol. A solution of appropriate concentration for preparation of the chromatogram results.

The second method is used for some types of chemically modified wool that do not hydrolyze well in 6*N* hydrochloric acid. Complete solution is affected by using 10 ml. of 1:1 formic acid:6*N* hydrochloric acid. A reaction temperature of 120° C. for 5 hr. should be used. This particular method is hazardous in that the tube is more likely to explode with considerable force during the heating step. The tube is cooled and the contents are handled in the same manner as described above.

Preparation of Chromatograms

Solutions: Two solvent mixtures [13] composed as follows are required.

Solvent A	*Volumes*
Ethanol	10
Butanol	10
Water	5
Propionic acid	2

Solvent B	*Volumes*
Butanol	10
Acetone	10
Water	5
Dicyclohexylamine	2

In addition a color developing reagent of the following composition is used.

	Volumes
0.1% Ethanolic ninhydrin	50
Collidine	2
Glacial acetic acid	15

Procedure: A 5-10 microliter sample of wool hydrolysate solution is deposited at a marked point 3 in. from the sides of an $18\frac{1}{4} \times 22\frac{1}{2}$-in. sheet of Whatman No. 1 filter paper. When the spot is dry, the sheet is hung with the sample up in a chromatographic cabinet arranged for descending chromatography. A standard of unchanged wool should be run with each group of samples. The atmosphere within the cabinet is saturated with respect to solvent A by placing several shallow dishes of the solvent on the floor of the cabinet. At least 5 hr. should be allowed for saturation to occur. A "run" is commenced by the introduction of Solvent A into each solvent trough. At 25° C. approximately 16 hr. are required for the solvent front to move within a few inches of the lower edge of the sheet. The sheet is removed, dried, rotated 90°, and returned to the cabinet where it is again mounted with the sample spot up. Using Solvent B, the atmosphere within the cabinet is saturated and the run is made. The sheet is removed and dried.

The sheet is sprayed until quite damp with the color developing reagent. Complete color development is obtained by placing the damp sheet directly into a 50° C. oven for 3 to 5 min. The position of each amino acid will be marked by a colored spot. Since the chromatogram discolors with time, it should be examined soon after development.

The location or R_f value of each amino acid on the chromatogram was determined by running each amino acid found in wool on a separate chromatogram. A typical chromatogram of a wool hydrolysate is shown in Figure 1. While the positions of both cysteic acid and lanthionine are marked, it should be noted that these do not often occur in the same hydrolysate.

Results

The minimum amount of cysteic acid detectable by this method is of the order of 0.5 μg. To determine the relationship between cysteic acid found and extent of damage, samples of wool were exposed for 24 hr. to varying concentrations of chlorine at a pH 4.5 and a temperature of 25° C. The change in the force required to extend the wet fiber 25% of its length was measured, and a chromatogram of the acid hydrolysate was prepared. By visual comparison, the percentage cystine converted was estimated. The results are summarized in Table I.

TABLE I. Effect of Chlorine on Wool

24 hr. Chlorine concentration (p.p.m.)	pH = 4.5 % Loss force at 25% extension	25° C. Estimated % cystine converted
2.0	3	5–10
4.0	10	10–20
6.0	19	20–30
10.0	45	30–45
20.0	69	45–65

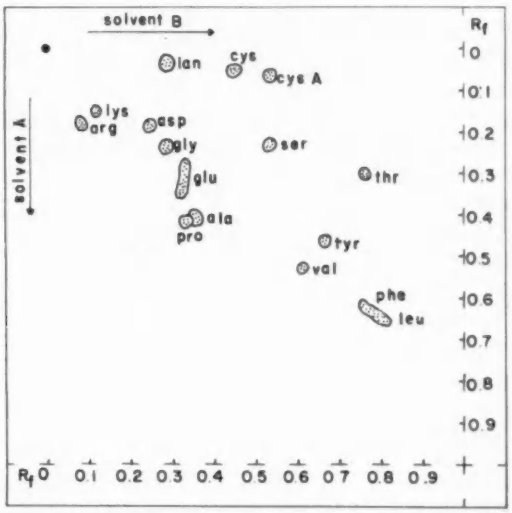


Fig. 1. Two-dimensional chromatogram of amino acids in wool exposed to chlorine oxidation and alkali.

Approximately 1 μg. of lanthionine gives a visible spot on the chromatogram. Samples of wool which had been exposed to solutions of varying pH at 25° C. for 24 hr. were hydrolyzed, and the amino acids were examined chromatographically. The forces required to extend the wet fibers of each sample 25% of their lengths were determined. The results are listed in Table II.

TABLE II. Effect of Alkali on Wool

24 hr. pH	% Loss force at 25% extension	25° C. Estimated % cystine converted
9.0	0	None
10.0	0	None
11.0	13	5–10
11.5	17	10–25
12.25	36	25–50

If some of the sample's history is known, the detection of damage by oxidizing agents can be more specific. In papermakers' felts, for example, chlorine is invariably the cause of detectable quantities of cysteic acid. While the water to which felts are exposed may contain peroxides, the quantities are insufficient to produce detectable cysteic acid or loss in fiber properties.

The described paper chromatographic procedure has been used repeatedly in the examination of wool textile samples for the detection of damage caused by alkali and oxidizing agents. It has advantages over other methods in that it is specific for the detection of damage by these materials and is not interfered with by other textile fibers. A minimum of working time is required. A further advantage is that chemical changes in the other amino acids composing wool are readily detected.

Acknowledgment

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INDUSTRIAL SECTION

Polyvinyl Alcohol as a Warp Size for Various Staple Yarns[1]

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Abstract

Polyvinyl alcohol has been evaluated as a warp size for cotton, Dacron[4] polyester staple yarn, and blends of Dacron staple with cotton and viscose rayon. Under simulated weaving conditions, superior sizing performance on all these yarns was given by completely hydrolyzed, high viscosity product. This type of polyvinyl alcohol also proved to be effective as an extender for various sizes based on starch or modified starch. The size formulations tested are described.

Introduction

Naturally occurring polymers, such as starch and gelatin, presently find widespread use as textile warp sizes. These materials, however, do not exhibit the required adherence to some of the more hydrophobic synthetic yarns. Synthetic polymers and starch derivatives must be used on yarns of this type. For example, filament nylon can be sized satisfactorily with polyacrylic acid and with polyvinyl alcohol. Filament Dacron polyester fiber can be sized with selected alkali-soluble vinyl acetate copolymers. Mixtures of polyvinyl alcohol and modified starches are effective sizes for spun synthetics, such as Orlon acrylic fiber,[4] Dacron, and others.

The object of this work has been to determine under simulated weaving conditions optimum formulations based on Elvanol polyvinyl alcohols[5] suitable generally for the sizing of cotton, Dacron staple yarn, and Dacron blended yarns. The sizing action of these polyvinyl alcohols has been compared whenever possible with that of Elvalan vinyl polymer,[6] Penford Gum 260,[7] and 40-fluidity starch. Elvanol polyvinyl alcohols have also been tested as extenders for starch. Softening agents used in these formulations include glycerine and Seycowax R.[8]

The types of yarn that were used are shown in

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[2] National Cylinder Gas Co., 840 N. Michigan Ave., Chicago 11, Ill.

[3] Electrochemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

[4] Manufactured by the Textile Fibers Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

[5] Product of the Electrochemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware. The following types were examined in this investigation.

Elvanol type	% Hydrolysis	Hoeppler viscosity of 4% water solution at 25° C., cp.
72–60	99–100	55–65
71–30	99–100	28–32
70–05	99–100	4–6
52–22	87–89	19–25
51–05	87–89	4–6

[6] An alkali-soluble vinyl acetate copolymer manufactured by the Electrochemicals Department, E. I. du Pont de Nemours and Co., Inc.

[7] Supplied by Penick and Ford, Ltd., New York, New York.

[8] Supplied by Seydel-Woolley and Co., Atlanta, Georgia.

Table I. As described in the Appendix, these yarns were sized in a laboratory slasher; they were then tested on a Southern Research Institute Shed Tester and on a Walker Abrader.

TABLE I. Description of the Yarn Used

Yarn	Av. staple length, in.	Cotton count	Twist, t.p.i.
Cotton	1 1/16	30	21Z
Dacron	1 1/2	15	14Z
65% Dacron 35% Cotton	1 1/4	18	14Z
60% Dacron 40% Viscose rayon	1 3/8	15	14Z

Discussion

A. *Cotton Yarn*

Large amounts of starch are consumed annually in the warp sizing of cotton. Though starch performs effectively in this application, it has certain deficiencies. One shortcoming is its high biochemical oxygen demand; as a consequence, a serious water pollution problem results from the disposal of wastes from the starch sizing and desizing operations. Other disadvantages include the extensive cooking required to prepare starch sizes and the necessity of using enzymes for efficient desizing.

The work reported here indicates that Elvanol 72–60, a completely hydrolyzed, high viscosity polyvinyl alcohol, is an effective warp size for cotton. This product has a very low biochemical oxygen demand, is incorporated readily into sizing formulations and does not require enzyme desizing. It has been used alone or as an extender for starch; in both cases, a superior performance at relatively low size pickup was observed under the testing conditions used.

The sizing compositions evaluated on 30's cotton yarn along with their Walker Abrader and shed values are listed in Table II. These formulations

TABLE II. Results of Tests on Cotton (30/1) Warp Yarn

Run No.	Size bath total solids %	Size pickup on yarn %	Strength lb.	Elongation %	Walker Abrader cycles to break av.	Shed %	Size formula, lb./100 gal.				
							Penick & Ford 40-fluidity starch	Elvanol polyvinyl alcohol 72–60	Elvanol polyvinyl alcohol 70–05	Elvalan (Na salt)	Seycowax R
Unsized	—	—	0.55	3.5	13	—	—	—	—	—	—
1	15.9	14.9	0.72	3.1	86	0.7	125	—	—	—	10
2	1.5	2.0	0.54	2.1	25	0.8	—	10	—	—	2
3	2.2	3.3	0.65	2.6	50	0.5	—	15	—	—	3
4	3.6	6.1	0.64	2.3	52	0.5	—	25	—	—	5
5	5.1	7.0	0.60	2.5	62	0.5	—	35	—	—	7
6	4.2	5.2	0.63	2.9	61	0.7	—	35	—	—	—
7	5.9	8.8	0.63	2.4	59	0.5	—	35	—	—	14
8	2.1	2.9	0.58	1.6	50	1.4	—	—	15	—	3
9	2.4	4.6	0.57	1.6	17	2.1	—	—	—	15*	3
10	10.3	10.2	0.65	2.3	65	0.7	65	15	—	—	6
11	9.4	11.0	0.68	2.4	81	0.6	65	7.5	—	—	6
12	7.2	7.6	0.68	2.3	53	0.5	40	15	—	—	5
13	10.3	11.6	0.64	2.1	73	0.6	65	—	15	—	6
14	9.3	10.2	0.67	1.9	66	0.5	65	—	7.5	—	5
15	6.9	10.5	0.67	2.4	70	0.6	40	—	15	—	5
16	10.6	13.1	0.65	2.3	76	0.7	65	—	—	15*	6
17	9.5	11.0	0.64	3.8	75	0.8	65	—	—	7.5†	6
18	7.4	10.5	0.61	3.2	60	0.7	40	—	—	15*	5
19	12.7	13.1	0.66	3.1	110	0.5	80	20	—	—	6
20	12.7	12.9	0.59	2.7	69	0.6	80	—	20	—	6
21	13.0	11.6	0.62	2.4	65	0.7	80	—	—	20	6
22	10.2	9.9	0.59	2.1	87	0.6	65‡	—	—	—	—

* 2 lb. Na_2CO_3 added.
† 1 lb. Na_2CO_3 added.
‡ 20 lb. Hercules CMC-CT—Medium viscosity added.

were based on Elvanol polyvinyl alcohols, Elvalan vinyl polymer, and 40-fluidity starch. Two control formulations, one prepared with 40-fluidity starch (Run 1), the other with starch and medium viscosity sodium carboxymethylcellulose (Run 22), also are described. Shed and Walker Abrader values reported for these two controls are similar to those values obtained with mill-sized yarn.

From the standpoint of both shed and abrasion resistance, the best results were obtained with a starch size which had been extended with Elvanol 72–60 polyvinyl alcohol (Run 19). The abrasion resistance was lower, but the shed value was essentially the same when this formulation was applied at a somewhat lower solids content (Runs 11 and 12). When other materials, such as completely hydrolyzed, low viscosity Elvanol 70–05 polyvinyl alcohol or Elvalan vinyl polymer, were used as starch extenders, the yarn exhibited less abrasion resistance than did either of the controls (Runs 13–18, 20, and 21). However, the shed values noted are entirely comparable with those obtained with the control formulations. As reported in Table III, the biochemical oxygen demand of the starch control size (Run 1) was lowered as much as 30% (Run 12) through the use of an Elvanol polyvinyl alcohol extender.

Good performances were also given by formulations based on Elvanol polyvinyl alcohols alone. Elvanol 72–60, the completely hydrolyzed, high viscosity polymer, again proved to be the most effective polyvinyl alcohol tested. Sizes prepared with this material operated at low pickup on the yarn with little shed (Runs 2–7); however, somewhat less abrasion resistance was imparted to the yarn than when a mixture of starch and the polyvinyl alcohol was used. As will be noted, the incorporation of Seycowax R into the formulation reduced the shed value somewhat (e.g., compare Run 6 with Runs 5 and 7). Of all the formulations listed in Table II, only those used in Runs 8 and 9 were considered unsatisfactory for weaving 30's cotton yarn. As noted in Table III, size formulations prepared with Elvanol polyvinyl alcohols alone have very low biochemical oxygen demands.

Though mixtures of starch and Elvanol 72–60 polyvinyl alcohol gave the best performance in this series of tests, there appear to be definite advantages in the use of a size containing only polyvinyl alcohol. With such a size, the wash waters containing the size can be discharged into city sewers and streams without the hazard of raising the biochemical oxygen demand appreciably. Enzyme desizing will not be required; instead, the polyvinyl alcohol film is removable by passing the yarn through a bath of warm water. Also, polyvinyl alcohol, once it has been applied to the warp yarn, can be converted into a loom finish by insolubilization with a thermosetting resin such as Zeset S Fabric Stabilizer.[9]

B. *Dacron Polyester 15/1 Spun Yarn*

Sizing problems encountered in the handling of Dacron polyester spun yarn differ somewhat from those met in the weaving of cotton. Dacron fiber is quite hydrophobic in nature and staple yarn prepared with this fiber has a fuzzy appearance. Such yarn has a pronounced tendency to shed fibers readily and also to felt during weaving. In spite of the fair abrasion resistance exhibited by this yarn, it must be warp sized before it will weave properly.

[9] Product of the Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

TABLE III. Biochemical Oxygen Demand of Cotton Warp Sizes

Run No.*	Size compositions, lb./100 gal.				Ratio starch/ modifier	Biochemical oxygen demand values	
	Starch	Vinyl polymer type	Amount	Seyco-wax R		1 Day p.p.m.	5 Days p.p.m.
1	125	—	—	10	—	160	4880
3	—	Elvanol 72–60	15	3	—	40	128
8	—	Elvanol 70–05	15	3	—	32	63
9	—	Elvalan (sodium salt)	15	3	—	112	608
10	65	Elvanol 72–60	15	6	80:20	85	3920
11	65	Elvanol 72–60	7.5	6	90:10	74	4000
12	40	Elvanol 72–60	15	5	70:30	58	3440
14	65	Elvanol 70–05	7.5	5	90:10	94	4320
17	65	Elvalan (sodium salt)	7.5	5	90:10	45	4560

* Refers to runs described in Table II.

Sizes now in use by the trade are based on materials such as Penford Gum 260, NuFilm R,[10] Ten-O-Film[11] and Elvalan. Elvanol 72–60 and 51–05 are widely used with these materials, the former product being preferred because it is somewhat more effective as a starch modifier.

Because there is need for improved sizes for Dacron spun yarn, formulations containing Elvanol polyvinyl alcohols and mixtures of these polyvinyl alcohols with Penford Gum 260 have been examined. As shown in Table IV, the best formulations tested on 15/1 yarn were prepared with Elvanol 72–60 (Runs 31 and 32). Except for somewhat reduced abrasion resistance, a comparable performance was given by the partially hydrolyzed, low viscosity polymer (Run 33). On the other hand, Penford Gum 260 or mixtures of this modified starch with Elvanol polyvinyl alcohols gave less satisfactory results. With Penford Gum 260 alone, a relatively high size pickup on the yarn was necessary before the yarn could be handled in the testing equipment. The three Elvanol polyvinyl alcohols listed in Table IV all proved to be effective extenders for Penford Gum 260, and the addition of these materials improved both the shed and Walker Abrader values (Runs 23–29). However, all yarn sized with formulations containing Penford Gum 260 was more prone to deposit a powdery residue when abraded. It should be noted that field testing has not as yet confirmed the superior performance indicated by this work for formulations containing only Elvanol 72–60. This may be due to the higher humidities normally used by cotton mills. In actual practice, mixtures of Elvanol 72–60 with starch appear to be more suitable.

[10] Supplied by National Starch Products, Inc., New York, New York.

[11] Supplied by Corn Products Refining Co., New York, New York.

C. *Dacron (65%)/Egyptian Cotton (35%) 18/1 Blended Spun Yarn*

Because completely hydrolyzed, high viscosity polyvinyl alcohol is indicated by our tests to be a superior size on both cotton and Dacron yarns, Elvanol 72–60 has been evaluated as a size on 65% Dacron/35% Egyptian Cotton 18/1 blended spun yarn. The results of this evaluation are shown in Table V.

The highest abrasion resistance and lowest shed were given by yarn sized with formulations containing Elvanol 72–60 and glycerine (Runs 41–43). Laboratory results were less satisfactory with Penford Gum 260 or mixtures of Penford Gum 260 and the polyvinyl alcohol (Runs 34–40). Though relatively low shed values were obtained with these latter formulations, the abrasion resistance imparted to the yarn was variable.

D. *Dacron (60%)/Viscose Rayon (40%)15/1 Blended Spun Yarn*

Because of a pronounced tendency to shed, viscose rayon spun yarn is more difficult to size for efficient weaving than cotton yarn. Blends of viscose yarn with Dacron or cotton tend to exhibit the same

TABLE IV. Results of Tests on Spun Dacron (15/1) Yarn Sized with Elvanol Polyvinyl Alcohol and Modifiers

Run No.	Size bath total solids %	Size pickup on yarn %	Strength lb.	Elongation %	Walker Abrader cycles to break av.	Shed %	Size formula, lb./100 gal.					
							Penford Gum 260	Elvanol polyvinyl alcohol 72–60	Elvanol polyvinyl alcohol 71–30	Elvanol polyvinyl alcohol 51–05	Glycerine	Seycowax R
Unsized	—	—	2.41	33	49	*	—	—	—	—	—	—
23	16.6	15.2	2.35	32	74	2.8	130	—	—	—	—	8
24	22.2	17.3	2.51	32	74	2.4	175	—	—	—	—	10
25	17.2	14.4	2.50	32	71	2.3	120	15	—	—	—	8
26	17.8	15.7	2.52	32	71	1.9	120	—	20	—	—	8
27	17.2	14.4	2.50	33	59	2.1	120	—	—	15	—	8
28	19.0	16.4	2.37	31	61	1.8	120	—	—	30	—	8
29	20.8	17.1	2.57	32	57	1.9	120	—	—	45	—	9
30	1.8	1.3	2.18	30	114	*	—	15	—	—	0.75	—
31	3.0	3.1	2.47	32	138	0.9	—	25	—	—	1.25	—
32	4.8	3.7	2.63	29	130	0.9	—	40	—	—	2.0	—
33	3.0	4.0	2.52	32	108	0.9	—	—	—	25	1.25	—

* Not possible to run on Shed Tester.

poor weavability. From experience at this laboratory, spun viscose rayon yarn should show acceptable weavability if its shed value is 1.5% or less.

In the work reported here, sizing formulations based on Elvanol polyvinyl alcohols as well as Penford Gum 260 were tested on 60%Dacron/40% viscose rayon 15/1 blended spun yarn. As shown by the data contained in Table VI, the most effective test performance was given by Elvanol 72–60 used with a small amount of glycerine (Runs 59 and 60). Good results were also obtained using Penford Gum 260 with any of the three types of polyvinyl alcohol listed in Table VI (Runs 46, 47, 49–55, and 57). Yarn sized with Penford Gum 260 alone exhibited

TABLE V. Results of Tests on Spun Dacron (65%)/Egyptian Cotton (35%) 18/1 Yarn Sized with Elvanol 72–60 Polyvinyl Alcohol and Modifiers

Run No.	Size bath total solids %	Size pickup on yarn %	Strength lb.	Elongation %	Walker Abrader cycles to break av.	Shed %	Size formula, lb./100 gal.			
							Penford Gum 260	Elvanol 72–60	Seyco-wax R	Glycerine
Unsized	—	—	1.25	4.5	27	*	—	—	—	—
34	12.7	12.9	1.26	3.5	31	0.7	100	—	6	—
35	18.9	18.0	1.34	3.4	32	0.8	150	—	8	—
36	17.8	17.3	1.46	3.8	28	0.9	120	20	8	—
37	20.2	16.9	1.25	3.0	30	0.6	120	40	8	—
38	12.1	13.4	1.53	5.3	22	0.8	80	15	6	—
39	13.9	14.4	1.44	4.1	26	0.5	80	30	6	—
40	11.5	12.5	1.50	4.9	24	0.6	60	30	6	—
41	1.8	3.0	1.33	4.0	33	0.4	—	15	—	0.75
42	3.0	4.1	1.31	3.6	33	0.3	—	25	—	1.25
43	4.8	6.5	1.40	3.7	37	0.2	—	40	—	2.0

* Not possible to run on Shed Tester.

TABLE VI. Results of Tests on Spun Dacron (60%) Viscose Rayon (40%) 15/1 Yarn Sized with Elvanol Polyvinyl Alcohols and Modifiers

Run No.	Size bath total solids %	Size pickup on yarn %	Strength lb.	Elongation %	Walker Abrader cycles to break av.	Shed %	Size formula, lb./100 gal.						
							Penford Gum 260	Elvanol polyvinyl alcohol				Seyco-wax R	Glycerine
								72–60	71–30	51–05	52–22		
Unsized	—	—	1.63	14.1	22	*	—	—	—	—	—	—	—
44	22.2	15.2	1.81	14.7	33	2.2	175	—	—	—	—	10	—
45	16.6	12.9	1.80	16.9	35	2.1	130	—	—	—	—	8	—
46	22.7	13.7	1.65	10.1	33	1.6	160	20	—	—	—	9	—
47	17.2	11.6	2.03	14.0	36	1.2	120	15	—	—	—	8	—
48	16.2	10.4	1.71	11.9	41	2.7	120	15	—	—	—	—	—
49	11.5	7.6	1.50	9.8	31	1.8	60	30	—	—	—	6	—
50	23.3	15.5	1.69	11.6	33	1.5	160	—	25	—	—	9	—
51	16.1	11.9	1.86	14.9	31	1.5	120	—	10	—	—	8	—
52	17.7	12.4	1.73	12.8	35	1.5	120	—	20	—	—	8	—
53	25.0	15.3	1.67	12.3	30	1.6	160	—	—	40	—	9	—
54	17.2	12.6	1.84	14.9	36	1.4	120	—	—	15	—	8	—
55	19.0	11.3	1.58	12.2	37	1.3	120	—	—	30	—	8	—
56	20.8	12.3	1.82	12.1	31	2.4	120	—	—	45	—	9	—
57	23.3	17.2	1.69	12.9	37	1.5	160	—	—	—	25	9	—
58	1.8	1.9	1.72	13.1	40	1.9	—	15	—	—	—	—	0.75
59	3.0	2.7	1.74	15.6	46	1.5	—	25	—	—	—	—	1.25
60	4.8	3.7	1.66	13.3	51	1.4	—	40	—	—	—	—	2.0
61	3.0	2.5	1.65	13.2	43	2.3	—	—	—	25	—	—	1.25

* Not possible to run on Shed Tester.

a greater tendency to shed than yarn sized with the majority of the formulations containing polyvinyl alcohol (Runs 44 and 45).

Acknowledgments

The assistance of Mrs. Gladys Milner, Miss Peggy Harrell, Miss Jeanette Esslinger, and Herbert P. Cox is gratefully acknowledged. They assisted in the experimental work and in the preparation of the data.

Appendix

Slashing

The size box of the Southern Research Institute slasher is made of stainless steel and is equipped with a perforated copper tube for the introduction of live steam. The delivery of steam is controlled by a recording thermostat which can be preset to give a wide range of size box temperatures. For the experiments reported here, the size box temperature was kept at 200° F. for starch-containing formulations and at 140° F. for formulations containing only vinyl polymers and glycerine.

In the size box are two stainless steel rolls with rubber-coated squeeze rolls above them. These rolls are driven by an electric motor through a Graham variable speed transmission. The yarns are fed into the slasher from four beams, each containing 42 ends. The sheet of yarns entering the size bath contains 168 ends lying side by side, as in standard mill practice. The wet yarn is carried through an electrically heated drying oven at 300° F., and then the dried yarns are separated from each other by means of split bars. Finally, the sheet of sized yarns is collected on a 4-in. Shed Tester spool.

Shed Tester

The SRI Shed Tester is essentially a miniature loom without the filling motion. It is equipped with a double set of harnesses, a reed and drop-wires for automatic stop motion when yarns break. In operation, the reed is caused to strike an impact bar simulating the beating up action of the reed in a standard loom. In each test, about 20 yd. of sized warp yarns is passed through the Shed Tester during the space of about 4 hr. The fiber and size that are abraded from the yarn drop to the bottom and are collected in an enclosed pan. This material, called shed, is weighed and the result is expressed as per cent of the weight of the total yarn tested. Previous results in this laboratory indicate that shed tests are reproducible within 0.1%.

Abrasion Resistance

The abrasion resistance of yarn is measured on the Walker Abrader manufactured by the U.S. Testing Company, Hoboken, New Jersey. This machine causes yarns to rub against each other until there is a break. The number of abrading cycles which cause a break is recorded. In practice, 24 strands of a given sample of yarn are mounted on the Walker Abrader. As each yarn breaks, the machine stops, and the number of cycles is read from a counter. After 12 consecutive breaks are recorded, the machine is stopped, and the remaining 12 strands are discarded. Four sets of abrasion data are thus obtained for each yarn sample. The grand averages are the averages of all 48 determinations for each yarn sample.

All shed and abrasion resistance tests were made in a conditioned room controlled at 70° F. and 65% R.H.

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Progress in Man-Made Protein Fibers[1]

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SIXTY years ago a man-made protein fiber was introduced but never found use in textiles because of its partial solubility in water. No really important improvements were made in the properties of the man-made protein fibers for about 40 years after their first appearance. In the same period regenerated cellulose fibers progressed from laboratory curiosities to the place where nearly every American owned some textile product made from rayon or acetate. There are probably many reasons for the disparity in development of these two classes of "half-synthetic" fibers, but as a chemist, I like to think that the chief reason is the great difference in chemical complexity of the proteins and cellulose. While cellulose consists essentially of a single chemical unit, glucose, the proteins are built of as many as 25 different amino acids which may be combined in thousands of ways into polymers ranging in molecular weight from 1,200 to hundreds of thousands.

The man-made protein fibers, along with the regenerated cellulosic fibers, occupy a position about halfway between the natural fibers (cotton, wool, silk, etc.) and the purely synthetic fibers (nylon, polyacrylics, polyesters, etc.). They are like the natural protein fibers in their moisture absorption, ease of dyeing, resilience, and warmth of hand, but unlike viscose rayon, which is chemically identical to cotton, the man-made protein fibers differ from wool in chemical composition. These fibers are not regenerated in the true sense of the word since the raw materials from which they were made are not fibrous materials. There is also a further distinction between the regenerated cellulosic fibers and the man-made protein fibers in that the further chemical step of curing, or reaction with cross-linking agents, is required to produce the protein fibers. We may say that the protein fibers are not regenerated but are generated and cured.

Fibers of a sort have been made from practically every protein which could be obtained in quantities sufficient for spinning experiments. However, the chief sources of proteins from which commercial fibers have been prepared are milk, peanuts, soybeans, and corn. Each of these sources yields a protein of different chemical composition and physical properties, and the fibers made from them, while alike in a general way, differ both chemically and physically. As Table I (adapted from Traill's compilation [14] indicates, the proteins of milk, peanuts, and soybeans contain numerous functional groups which give the proteins, as well as the fibers made from them, relatively high chemical reactivity. These proteins are easily hydrated, at least partly soluble in water, and also in solutions of acids or bases. Fibers obtained from them partake of these properties. Although they are not soluble in water or aqueous solutions, the fibers swell greatly and do not withstand treatment with hot solutions of common chemicals. Zein, on the other hand, contains a relatively high proportion of inactive, nonpolar, hydrocarbon residues along its polypeptide chain, and these render the protein naturally somewhat hydrophobic. This protein is unusual also in that it is insoluble in water and acid solutions and is soluble in alcohols and certain other organic solvents. Consequently, zein fibers are less easily swollen by and are more resistant to common chemicals.

TABLE I. Amino Acid Composition of Proteins

(Grams of Amino Acid per 100 g. of Protein)

	Type of amino acid			
Protein	"Inactive"	Acidic	Basic	Sulfur cont.
Casein	44.24	28.73	15.43	3.90
Peanut	22.88	36.05	18.71	2.82
Soybean	30.49	23.32	13.50	3.00
Zein	50.08	39.00	2.40	3.21
Wool	34.60	23.27	11.90	12·15

An important difference between the proteins which have been used in the manufacture of fibers and wool is the content of the sulfur-containing

[1] Presented to the Textile Section, Gordon Research Conferences, American Association for Advancement of Science, New London, New Hampshire, July 14, 1955.

amino acids, principally cystine. This disulfide amino acid has been shown by Harris and his coworkers [7] to be of prime importance to the excellent mechanical properties of wool. Duplicating by other means the role of cystine in wool has been one of the major problems of the man-made protein fiber industry.

The majority of the man-made protein fibers which have been on the market have failed to meet the requirements of the textile industry primarily because of their inferior resistance to water and to hot liquids encountered in textile processing. Table II [9] showing the dry and wet tenacities of various protein fibers compared with wool, indicates that the zein fibers are the best man-made protein fibers yet produced.

TABLE II. Dry and Wet Tenacities of Protein Fibers

Fiber	Dry tenacity g./den.	Wet tenacity g./den.	Wet tenacity % of dry
Wool 50's	1.2	0.90	75
Zein*	1.2	0.75	62
Peanut protein†	1.0	0.60	60
Casein†	0.8	0.40	50
Soybean protein†	0.7	0.35	50
Casein*	0.7	0.30	43
Peanut protein*	0.8	0.30	38

* Commercial.
† Prepared in laboratory.

The modern history of the man-made protein fibers begins with the work of Antonio Ferretti which culminated in the production in 1935 of a casein fiber called "Lanital" by Snia Viscosa. Fibers from casein followed in many countries: Tiolan in Germany, Corgan in Belgium, Casolano and Lactofil in Holland, Polan in Poland, Fibrolane in England, Merinova in Italy, and Aralac in the United States. Of these, only Fibrolane, Merinova, and Lanital in Belgium, are now being manufactured.

Soybean protein fibers have been made in many countries, primarily those in which soybeans are an important agricultural product. A Japanese soybean protein fiber called "Silkool" has been reported, and in the United States brief commercial production of soybean protein fibers was carried out by the Drackett Company in 1943.

Imperial Chemical Industries, Ltd., of England presently produces a peanut protein fiber, Ardil, and has conducted extensive research in the protein fiber field.

Based on the evaluations of proteins for fiber production carried out in the Regional Laboratories of the United States Department of Agriculture, a zein fiber was developed and manufactured in commercial quantities by the Virginia-Carolina Chemical Corporation in 1948. Under the trade-mark, "Vicara," this fiber has been manufactured in increasing quantities since that time.

Manufacture of Zein Fiber

The manufacture of the various protein fibers follows a common pattern. Since I have been more intimately concerned with zein fibers, I shall describe their manufacturing process specifically rather than attempt to cover the field. The process which produces zein fibers properly starts with the extraction of zein from corn gluten meal, a by-product of the wet milling of corn kernels, with isopropyl alcohol. The zein is produced in the form of a pale yellow powder. Typical molecular properties of zein used in fiber manufacture are shown in Table III [11]. While there is no real proof of the idea, most investigators believe that the same type of relationship between molecular weight and fiber strength exists for the proteins, as has been shown in the case of the synthetic and cellulosic fibers. In the plot of tenacity versus degree of polymerization from Mark [12] (Figure 1), the proteins probably

TABLE III. Molecular Properties of Commercial Zein

Molecular weight	
a. Sedimentation-viscosity	28,000
b. Osmotic pressure	28,500
Molecular dimensions, Å	226/17.4
"Degree of polymerization"	240

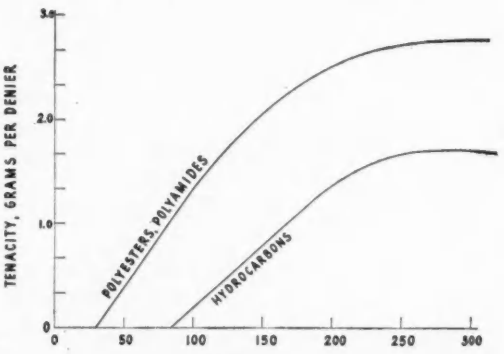

Fig. 1.

fall somewhat above the hydrocarbons. In agreement with this theory, it may be noted that fibers have been prepared from pure zein which have a tenacity of 1.5 g./den. probably a maximum with zein of the molecular weight previously indicated.

The zein powder, after blending to ensure uniformity, is dissolved in an aqueous alkaline solution. In this solution several changes occur. The viscosity of the solution increases as time passes, and eventually a solid gel is formed. Ultracentrifuge studies of zein spin solutions made by Dr. Carl Likes [11] at the Virginia Institute for Scientific Research show that strong aggregation of the protein molecules takes place probably after some initial unfolding of the molecules baring hydrogen bonding sites. Figure 2 shows a typical photograph of the moving boundaries of polymer material 9 min. after the ultracentrifuge rotor reached speed. Both aggregated and unaggregated material show as separate peaks in the diagram. Table IV gives typical results

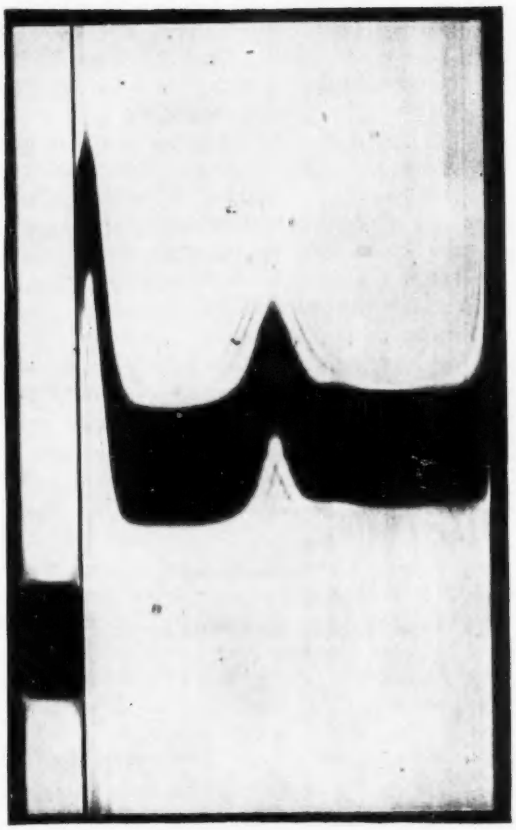

Fig. 2.

TABLE IV. Ultracentrifuge Analysis of Zein Spin Solution

Age, hr.	$S^{0}_{20} \times 10^{13}$		Concentration, wt. %	
	Peak 1	Peak 2	Peak 1	Peak 2
3	29.7	2.71	0.29	0.71
94	29.4	1.59	0.56	0.44

of ultracentrifuge analysis of zein spin solutions obtained from photographs similar to the one shown. (The sedimentation constant is a measure of the speed with which the particles sediment under the influence of the rotation, and, of course, the heavier the particle the faster it moves.) We have obtained qualitative evidence that the aggregates are somewhat linear in structure, or orientable, from streaming birefringence studies made with Dr. Joseph Foster at Iowa State College. At very high rates of shear zein shows modest streaming birefringence, but zein spin solutions of equivalent concentration show marked birefringence at low shear rates. Very approximate calculations showed approximately tenfold increase in particle length.

After the proper amount of ageing, the filtered and deaerated zein solution is extruded through spinnerets into an acid coagulating bath where fibers are formed. The output of many spinnerets is collected in the form of a tow which may contain as many as 270,000 filaments. The tow is then conveyed to "precuring" tanks where an initial "hardening," or reaction with formaldehyde, conditions the fibers for the next operation, stretching. The amount of stretch given the fibers at this point determines to a great extent the dry strength of the ultimate fiber, as Table V shows. As the amount

TABLE V. Effect of Stretch on Strength

Stretch, %	Tenacity, g./den.	Birefringence
126	0.58	0.003
187	0.58	0.002
259	0.68	0.006
353	0.92	0.009

of stretch increases, the strength increases. This relationship is a common one for the manufacture of fibers from any high polymer, but distinct differences between the polymers begin to show up at this

stage. In the case of lean, symmetrical chain molecules, such as make up nylon, close approach of the chains to one another allows crystallization, and the strong forces in the crystallites are disrupted only by strong reagents. Thus, the synthetic and cellulosic fibers are essentially completely formed after stretching. Not so with the protein fibers. The molecules from which they are made are unsymmetrical and bristling with side chains of a variety of length and structure, and in every case, the attraction between chains is sufficient to induce only a modest degree of crystallization. As a matter of fact, of the commercial protein fibers only the zein fiber shows sufficient crystallinity to produce a slight reinforcement of the amorphous β-keratin x-ray diagram common to the protein fibers. Consequently, unless some further steps are taken to stabilize the structure, water or other polar liquids can easily penetrate and weaken the fibers. For example, the zein fiber mentioned, which has a dry strength of 1.5 g./den., has a wet strength of about 0.2 g./den.

All of the commercial man-made protein fibers have, after stretching, the so-called "beta," or stretched out configuration of the protein molecules, as contrasted to wool, which possesses the "alpha," or folded configuration. Some of the desirable elastic properties of wool have been attributed to this structure. On the basis of his work with synthetic polypeptides, C. H. Bamford of Courtaulds, Ltd. has suggested [1] the arrangements of the polymer chains shown in Figure 3 for the two types of structure. An interesting sidelight on how differences in molecular arrangement can affect the physical properties of the polypeptides is provided by Bamford's demonstration that certain polypeptides cast into films from solvents which yield primarily the β-form are soluble in water, while the same polymer in the α-form is insoluble in water and soluble in hydrocarbon solvents. So far, however, no one has reported the same behavior with the more complex industrial proteins.

In order to improve the wet strength and chemical resistance of the man-made protein fibers, it is necessary to introduce chemical cross-links between the protein molecules. Many chemicals have been used for this purpose, but the simplest and most effective reagent is formaldehyde. It is the general consensus that these cross-links are formed between the reactive groups which terminate the side chains of the constituent amino acids and that the effectiveness of the linkages depends in large part on the nature of the chemical groups which are connected. As was shown in Table I, casein, peanut protein, and soybean protein contain a rather substantial quantity of amino acids with basic side chains, primarily lysine, which has a terminal amino group. Formaldehyde reacts quickly with amino groups of proteins in neutral or basic solutions to form cross-links with various other reactive groups, as Figure 4 indicates; but these cross-links are quite easily broken in solutions of lower pH [2, 5]. Hence, fibers made from these proteins have a tendency to become jellylike when they are dyed with strong acids, as is customary with wool. Zein, on the other hand, contains relatively few basic amino acids and no lysine, but it has a high proportion of acid amide groups contributed by its high content of glutamine and asparagine. Formaldehyde cross-links between amide groups are formed in strong acid solution (Figure 5), and thus are rather stable to the usual condi-

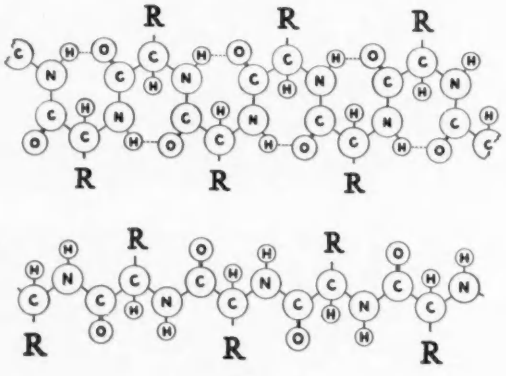

Fig. 3.

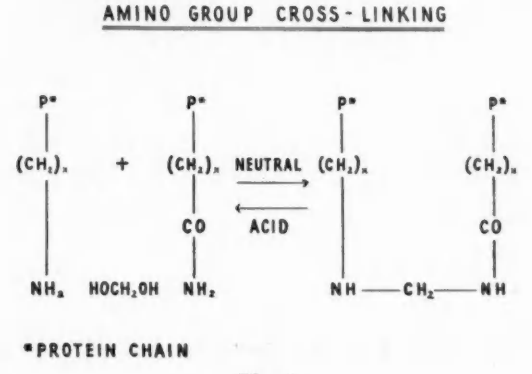

Fig. 4.

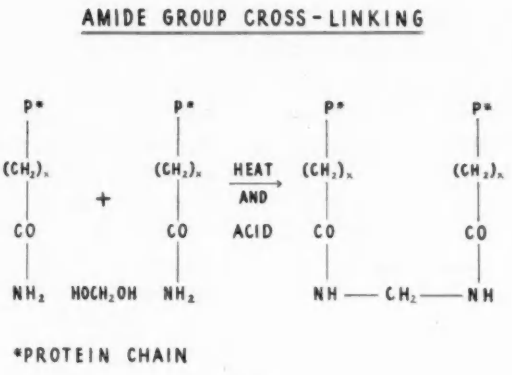

Fig. 5.

tions of acid dyeing. Zein fibers, in which the major portion of the cross-links is of the amide type, are, in fact, affected only modestly by acid dyeing.

After the final hardening, or cross-linking, of the fibers is accomplished, excess chemicals are washed out, the fibers are treated with a lubricant to assist in textile processing, dried, crimped, and cut into the desired staple length.

As Tables VI, VII, and VIII show, the man-made protein fibers, especially the commercial zein fibers, rank with wool in mechanical properties under the usual conditions of textile testing (65% R.H., 70° F.). The superiority of wool in the wet state is evident, however, particularly in the properties of work and tensile recovery. It should be pointed out that the rather high figures for wet recovery shown by the peanut protein fibers is due to their great swelling. They show the same type of rubberlike recovery in the wet state that rayon fibers swollen in caustic do.

Harris and Brown [6] have shown that the stability of the structure of wool and man-made protein fibers in the wet state is dependent on the presence of primary valence cross-linkages. To theorize a bit, two things appear to operate to give wool its superiority in wet recovery properties: (1) the location of the disulfide cross-links, and (2) the length of these cross-links. Cross-linkages in the man-made protein fibers are of necessity put into the fiber structure helter-skelter, while the wool structure is organized as it grows. When wool is carefully dissolved by rupture of its disulfide bonds and is then regenerated, the resultant fibers if anything are poorer in properties than the man-made fibers. The cystine linkages in wool are made up of four atoms while the most probable linkages in the man-made protein fibers are nine atoms long. Hence, it is plausible to say that their fiber structure should be more yielding and less elastic in the wet state than wool.

Dyeing Properties

The parallel between man-made and natural protein fibers has been widely quoted in the dyeing field, and in general, well-known techniques of dyeing wool are applicable to the dyeing of man-made protein fibers. This is to say, zein, peanut protein, and casein fibers are colored by the same classes of dyestuffs which color wool, and dyes on these fibers have about the same fastness properties as the same dyes exhibit on wool. But this does not mean that

TABLE VI. Strength and Toughness of Protein Fibers

	Tenacity, g./den.		Work to stretch, 10^6 ergs/cm.^{3}			
			5%		20%	
Fiber	Dry	Wet	Dry	Wet	Dry	Wet
Wool	1.20	.90	23	6.9	145	61
Zein	1.20	.75	24	8.8	136	65
Peanut protein	1.03	.58	21	5.0	110	37

TABLE VII. Flexibility, Compliance, and Liveliness of Protein Fibers

	% Ultimate elongation		Compliance ratio den./g.	Young's modulus g./den./%	
Fiber	Dry	Wet	Dry	Dry	Wet
Wool	38	50	1.3	0.25	0.11
Zein	37	33	1.5	0.27	0.12
Peanut protein	36	33	1.8	0.29	0.07

TABLE VIII. Resiliency Properties of Protein Fibers

	% Work recovery				% Tensile recovery			
	5% Ext.		20% Ext.		5% Ext.		20% Ext.	
Fiber	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Wool	47	60	17	52	65	97	35	98
Zein	44	27	18	28	67	46	32	42
Peanut protein	27	33	14	36	50	56	27	55

no adjustment of technique or no particular choice of dyestuff is required to dye wool and zein fiber blends in union shades. There are quite definite differences in the chemical compositions of the two proteins which show up prominently in the dyeing of mixtures of the two fibers. The practical dyer is able by the exercise of his ingenuity to dye blends of the two fibers in practically any shade. In the laboratory using standardized methods, Sookne and Saxon [13] have found that when wool and zein fibers are dyed together with certain acid dyestuffs, the wool will take up most of the dye, leaving the zein fibers lighter in shade. This disparity in dye uptake is partly a matter of rate of dyeing, since the dye strike on wool occurs at a lower temperature than it does on zein fibers, but this is not the whole story. There is definitely no deficiency of charged dye-binding sites in zein fibers. The number of basic groups in zein fibers available for electrostatic binding of dye anions is about one-fourth the number in wool, but it is still far in excess of the requirements for commercially used concentrations of dyes.

Alone or in blends with fibers other than protein, zein fibers readily absorb several percentages of the same acid dyestuffs which dye wool preferentially. The difference between the dyeing behavior of zein fiber and wool, we believe, lies primarily in the electrostatic character of the proteins. In wool the ratio between potentially negatively charged groups which will repel anionic dyes and potentially positively charged groups which will attract these dyes is about 1.5 to 1. This same ratio for zein is about 4 to 1. Therefore, we think that dyes in which the anion or negatively charged portion is the color carrier will be preferentially attracted to the more positively charged wool fiber. Conversely, cationic, or positively charged dyes should color zein fibers somewhat darker than wool, and indeed, they do. This is a rather mixed blessing since the basic dyestuffs have only slightly better fastness on zein fibers than on wool. The neutral disperse or acetate dyestuffs have excellent affinity for the protein fibers, but here again, their fastness on zein fibers is just a little better than it is on wool. One particular class of dyestuffs seems to give the most foolproof union dyeings of zein fiber and wool blends . . . the neutral dyeing premetalized dyes. These dyes are neither anionic nor cationic, and, hence, fiber charge effects do not influence their uptake.

Applications

The man-made protein fibers have so far been used primarily in blends in apparel fabrics. In certain industrial applications, such as hot oil filtrations and high temperature lubrication where acid and heat resistance are of prime importance, 100% zein fiber fabrics have performed in a superior way, as Table IX [3] indicates they should. The cross-linked structure of the protein fibers confers on them excellent resistance to heat. They do not melt, and as a matter of fact, zein fibers lose in strength only above 350° F. The same feature of cross-linking gives the protein fibers excellent resistance to organic solvents of all kinds. The fibers cannot be dissolved in any reagent which does not attack the primary valence linkages. One measure of the chemical inertness of zein fibers is that sodium hydroxide, which reacts with wool and dissolves it, is used to separate wool and zein fibers in quantitative analysis of blends [15].

TABLE IX. Effect of Alkali, Heat, and Acid on "Vicara" Fabric

Treatment	Strength, lb.	Change, %
6 hr. at 275° F.		
With 1% NaOH	120	− 8.4
With 1% H_2SO_4	132	+ 0.8
1% H_2SO_4, 30 min. at		
275° F.	135	+ 7.5
300° F.	141	+12.2
325° F.	143	+13.6

$$F = \frac{KMD^4}{L^3} \qquad (1)$$

F = force to produce a given bend, within elastic limit
K = proportionality constant
M = modulus of elasticity
D = diameter of filament (considered to be round)
L = length of free span

The main field of use of the man-made protein fibers has, however, been in wearing apparel and household fabrics, as is true of the natural protein fibers. In these end uses the fibers make definite contributions to fabrics containing them. Lyman Fourt [4] has very ably correlated protein structure with fiber and fabric properties and much of what I have to say on the properties of fabrics containing the man-made protein fibers derives from his work. While I can pose only as an interested amateur in

the field, I would like to examine with you one or two of the major properties of fabrics containing the man-made protein fibers and to attempt to correlate these properties with the mechanical properties of the fibers.

One of the chief contributions of the zein fibers to fabrics is luxuriousness of hand. This is a property shared by all of the very fine protein fibers, such as cashmere and fine wools. There are at least two aspects of the luxurious feel which can be attributed to the mechanical properties of the protein fibers. Of course, any fine fiber can give surface softness to a fabric, but it is not this luxury touch that will be considered here. Figure 6 shows the stress-strain or load versus elongation diagrams of several fibers. From this it is immediately apparent that the wool-like protein fibers are considerably different from the other fibers shown in their response to stretching forces. Cotton resists increase in elongation with about the same force requirement for unit elongation, for example, and nylon actually work hardens with increasing elongation. The wool and zein fibers have a stiffness limit, below which they resist change at about the same rate or modulus as the other fibers, but above which they elongate with very little additional force. However, this is not yielding to break as there is a final hardening in these fibers also.

First let us consider the initial portion of the stress-strain diagram of the fibers, the portion covering elongations less than 5%. In Equation 1 that is shown above, considering the length of the fibers to be constant and the same, it can be seen that the stiffness of fibers is directly proportional to the

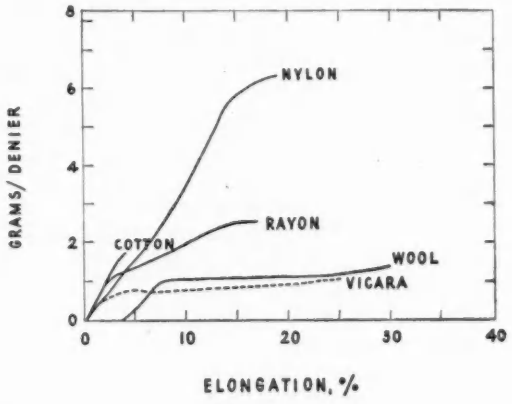

Fig. 6.

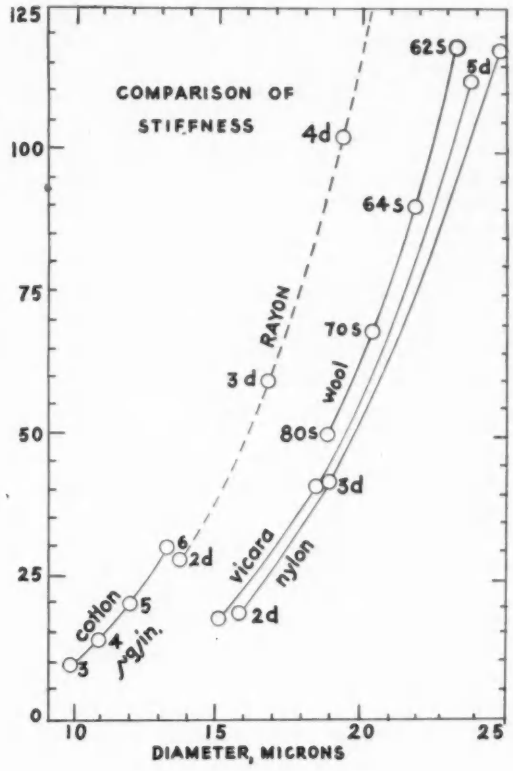

Fig. 7.

product of their modulus and the fourth power of the fiber diameter. Thus, the protein fibers and nylon, which have comparative initial moduli, are about the same in their initial response to strain if they are of the same size, as Figure 7 indicates. The chart also shows that the cellulosic fibers, cotton and rayon, are, for the same size fibers, considerably stiffer in this aspect of fabric hand than the other fibers. It is in response to greater deformations that the protein fibers show very definite differences from other fibers, and this has been ascribed by Hoffman and Beste [8] to the diminishing modulus of wool and the man-made protein fibers. These workers have used the term "compliance ratio" to characterize this additional characteristic possessed by the protein fibers, that of yielding rapidly to small increases in force once the yield point has been exceeded. Thus, fabrics containing the protein fibers are first springy and full when they are crushed in the hand, and then become soft and yielding as

the pressures are increased. Fourt [4] has described this aspect of hand as "deep softness," and it is an apt description.

A further contribution of the man-made protein fibers to fabrics is the recovery from creasing and wrinkling which these fibers bring to blends, particularly blends with the cellulosic fibers. Such behavior has been related to the tensile and work recovery properties of the protein fibers by several investigators, Hoffman and Beste [8], and Krasny and Sookne [10]. Table X shows one of the measurable results of the superior recovery properties of fabrics containing one of the man-made protein fibers. None of the fabrics listed here had been given a crease-resistant finish. The range of values for crease recovery was obtained from several different weights and constructions of the same blend.

TABLE X. Crease Recovery of "Vicara" and Rayon Blends

Fabric composition		Crease recovery
Vicara, %	Rayon, %	Monsanto, %
100	—	80–85
50	50	73–78
30	70	72–75
25	75	70–78
—	100	50–60

In this day of such a multiplicity of fibers, it is perhaps rather dangerous to predict the future of any particular fiber. However, I do believe that there is a definite place in the textile industry for the man-made protein fibers, particularly since their properties have now reached an acceptable level. These fibers fit into a niche which up to this point has been occupied only by the scarce and expensive natural fibers. The man-made protein fibers offer a luxuriousness in fabrics which is not otherwise economically obtainable. I believe that in the sportswear, shirting, robe, and blouse fields we will see more and more use of the man-made protein fibers because of the unique properties these fibers possess. Likewise, I believe that all types of knitwear from sweaters to T-shirts will be made increasingly from the man-made protein fibers. If practical luxury at moderate cost is a selling point in textiles, then the man-made protein fibers will be with us for the long haul.

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The Geometry and Properties of Two-Bar Tricot Fabrics

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Abstract

A study was made of the geometry of 97 two-bar tricot fabrics knit of several deniers of acetate and viscose filament yarns knit with different courses per inch and runner ratios. Relationships were derived from the observed data of stitch length, diameter of yarn, runner ratios, wales and courses per inch, breaking strength, elongation, and bursting strength.

IN previous papers [1 through 3] the authors have published data relating the stretching and shrinkage of plain knit fabrics in laundering to their geometry. The research reported here extends the work to 97 two-bar tricot fabrics of eight yarns knit with various runner ratios and courses per inch. Relationships of some of the construction factors, such as stitch length and runner ratio, to shrinkage, strength, and elongation were determined.

Materials

The tricot fabrics studied were knit under controlled conditions in the Textile Research Department of the American Viscose Corporation. They were made on a 28-gauge two-bar tricot machine; the pattern used was: front bar 2-3, 1-0; back bar 1-0, 1-2 (Figure 1). The yarns were dull filament of 55-, 75-, 100-, and 150-den. acetate and of 50-, 75-, 100-, and 150-den. viscose (Table I).

Forty-six fabrics were knit of the eight yarns with a 4 to 3 runner ratio.[1] Fifty-one additional fabrics were knit of the 75-den. yarns with other runner ratios ranging from 11/10 to 8/5.

Some of the yardage of the gray goods was reserved for the study of the unfinished goods. The remainder was scoured with synthetic detergents and dried on a pin tenter at 220° F. The tenter frame was set at 56 in. for drying all the fabrics except those knit of 150-den. yarns. These were dried with the frame set at 67 in.

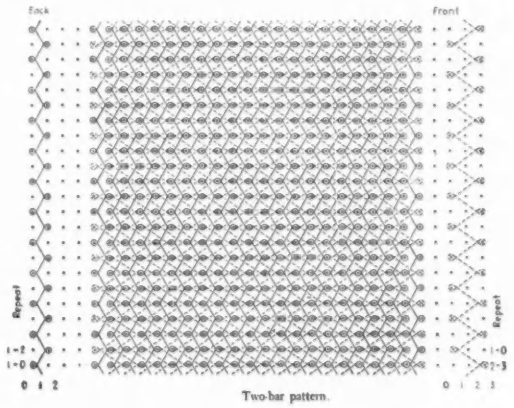

Fig. 1. Two-bar pattern for tricot fabrics showing front and back runners. (Courtesy of American Viscose Corporation.)

TABLE I. Number, Twist, and Diameter of Yarns

Yarn	Number (conditioned), den.	Twist (direction and turns per inch), number	Diameter, 0.001 in.
Acetate			
55/14	54.5	Z 0.1	5.742
75/20	75.9	Z 0.5	6.555
100/28	100.5	Z 0.3	7.909
150/41	151.2	Z 0.7	10.228
Viscose			
50/20	52.6	Z 0.9	4.789
75/30	79.3	Z 2.5	5.659
100/60	103.4	S 2.1	6.719
150/40	162.2	Z 2.2	7.850

[1] Runner is the inches of yarn in 480 stitches; runner ratio is length of front runner divided by length of back runner.

Method

The construction of the tricot fabrics was analyzed by the method outlined by Eshleman [4] and Nelson [5]. Three specimens of cloth approximately 12 × 6 in. were used in measuring stitch length and runner ratio. Five parallel lines 1 in. apart were marked off with ink, perpendicular to the wales on each specimen. Two adjacent yarns of the back bar and one of the front bar were raveled simultaneously and measured for each of the 1-in. distances. From the data for length of yarn and number of courses per inch, the stitch lengths and runner ratios were calculated.

The diameter of the yarns, weight of the cloth, wale and course counts were determined as described in a prevous study [1].

For shrinkage determinations, the fabrics were laundered at 100° F. five successive times and screen-dried between launderings, as previously described [2]. Two sets of three specimens were used: one was laundered without preliminary treatment; the other was given a manual relaxation treatment before laundering to remove distortion.

The relaxation treatment consisted of soaking the fabric in warm water for 2 hr. and then stretching or shrinking it to approximately the dimensions assumed by a similar area of laundered fabric. The material was then floated over a screen and allowed to dry without tension.

The grab method was used in measuring the strength of cloth lengthwise and crosswise. Specimens, 6 × 4 in., were broken with a pendulum-type Scott Tester. Bursting strength was measured by using a Model C Mullen Tester.

Results and Discussion

Length of Stitch and Weight

The equations for stitch length were expressed as a function of the diameter of the yarns and wale and course spacings. These were analogous to the equation

$$l = 2p + w + 5.94d$$

which was derived by Peirce for plain knitting [6].

The equations for the measured stitch length of the tricot fabrics (Tables II and III) varied as follows:

	Acetate	*Viscose*
from	$l_1 = 2p + 2.5w + 3.92d$	$l_1 = 2p + 2.5w + 4.28d$
to	$l_1 = 2p + 2.5w + 7.21d$	$l_1 = 2p + 2.5w + 8.47d$
and from	$l_2 = 2p + w + 7.53d$	$l_2 = 2p + w + 8.73d$
to	$l_2 = 2p + w + 5.19d$	$l_2 = 2p + w + 5.52d$

In these equations l_1 is the stitch length for the front runner, l_2 the stitch length for the back runner, p course spacing, w wale spacing, and d the diameter of the yarn. The coefficients of d in the equations for stitch length of front runner in the acetate and viscose fabrics increased from 3.92 to 7.21 and from 4.28 to 8.47, respectively, as the runner ratio increased from 11/10 to 8/5. These same coefficients decreased from 7.53 to 5.19 and from 8.73 to 5.52 in the equations for stitch length of back runner as the runner ratio increased.

The following equations express the sum of the stitch lengths for the front and back runners:

Acetate

$$l_1 + l_2 = 4p + 3.5w + 11.75d$$

Viscose

$$l_1 + l_2 = 4p + 3.5w + 13.52d$$

and the coefficients of d do not vary as the runner ratio increases. The sum of the stitch lengths, $l_1 + l_2$, is the length of yarn in the unit cell of the tricot fabric.

The equation used to calculate the weight W per unit area of cloth is analogous to the equation derived by Peirce for plain knitting [6] as

Plain

$$W = \frac{lg}{wp}$$

Tricot

$$W = \frac{(l_1 + l_2)\,g}{wp}$$

In the equations $l_1 + l_2$ is the yarn in unit cell or the sum of the stitch lengths for the front and back runners, g the weight per unit length of yarn, w the wale spacing, and p the course spacing. The calculated weight showed good agreement with that obtained by weighing a known area.

TABLE II. Wales and Courses per Inch and Stitch Length of Tricot Fabrics Knit of Four Yarns with a 4/3 Runner Ratio

Fabrics	Yarn, den.	Wales/ in., number	Courses/ in., number	Length of stitch: Front runner, 0.001 in.	Length of stitch: Back runner, 0.001 in.
Acetate					
1	55	43.2	54.9	125.3	93.0
2	55	42.6	49.9	128.1	96.2
3	55	42.3	48.3	130.3	99.0
4	55	42.5	45.7	136.2	102.2
5	55	42.2	44.1	141.0	105.6
6	55	41.8	41.2	145.1	109.1
7	55	41.9	39.0	149.5	111.5
8	75	41.5	53.0	131.7	99.2
9	75	41.5	49.4	133.6	100.8
10	75	41.1	47.2	139.2	105.8
11	75	40.8	44.2	149.7	110.4
12	75	40.8	41.7	155.2	112.6
13	100	40.1	53.0	138.9	104.2
14	100	41.6	48.5	144.0	108.8
15	100	41.8	45.5	147.2	110.6
16	100	41.6	43.9	151.8	115.8
17	100	41.4	41.7	159.1	118.9
18	150	35.6	43.2	164.9	117.9
19	150	35.7	39.6	170.5	131.8
20	150	35.5	35.6	184.3	136.9
21	150	37.8	32.7	186.0	142.6
22	150	35.1	30.6	197.4	151.1
23	150	34.2	28.2	211.0	158.3
Viscose					
24	50	41.8	59.2	114.3	85.0
25	50	41.0	54.6	117.9	89.8
26	50	42.0	52.2	121.6	90.7
27	50	40.9	51.1	122.5	92.6
28	50	40.8	46.5	128.1	95.9
29	50	41.4	44.6	134.8	101.3
30	50	41.0	42.4	138.1	100.9
31	50	41.7	40.3	142.4	105.2
32	75	41.5	49.5	133.1	100.0
33	75	42.0	46.7	136.2	101.1
34	75	42.2	46.0	141.9	104.8
35	75	41.5	44.2	144.3	107.8
36	75	40.7	41.6	153.1	112.1
37	100	41.2	51.8	137.2	102.8
38	100	41.2	47.2	143.5	107.3
39	100	41.6	43.4	147.6	111.0
40	100	40.6	42.4	151.7	113.8
41	100	40.1	41.3	157.8	118.6
42	150	35.4	46.1	160.1	118.5
43	150	34.4	42.4	169.5	124.5
44	150	35.0	37.4	179.2	134.2
45	150	34.6	34.6	186.0	138.8
46	150	33.3	32.7	199.1	147.6

TABLE III. Wales and Courses per Inch and Stitch Length of Tricot Fabrics Knit of 75-Den. Yarns with Various Runner Ratios

Fabrics	Runner ratio	Wales/ in., number	Courses/ in., number	Length of stitch: Front runner, 0.001 in.	Length of stitch: Back runner, 0.001 in.
Acetate					
1	9/7	41.6	55.4	130.2	100.9
2	5/4	41.2	55.7	126.8	100.0
3	7/5	43.6	54.1	132.6	95.1
4	3/2	43.7	55.7	136.8	91.3
5	6/5	42.4	50.7	129.6	108.5
6	5/4	42.4	50.5	131.5	106.0
7	7/5	42.5	50.6	139.6	99.0
8	3/2	43.7	51.7	142.3	95.0
9	11/10	42.2	46.9	128.2	116.8
10	6/5	42.0	47.3	133.4	112.2
11	5/4	42.7	47.2	136.2	107.7
12	7/5	42.3	49.1	141.6	101.6
13	3/2	43.2	50.2	146.0	97.6
14	11/10	42.8	42.3	131.1	119.4
15	6/5	42.4	44.0	136.1	113.8
16	5/4	41.8	44.3	139.3	111.9
17	7/5	42.3	45.4	146.1	104.6
18	3/2	43.3	46.7	148.7	101.4
19	11/10	41.8	41.2	133.8	121.4
20	6/5	41.7	41.9	139.1	116.7
21	5/4	41.7	42.1	142.9	114.3
22	7/5	42.8	43.2	150.2	106.6
23	3/2	42.4	44.6	153.3	102.5
Viscose					
24	6/5	42.6	52.9	124.2	105.3
25	5/4	42.9	50.5	126.8	104.4
26	7/5	42.8	50.6	133.7	97.4
27	3/2	41.9	53.4	137.4	92.9
28	8/5	41.7	57.0	139.0	89.0
29	11/10	41.8	47.9	121.6	111.2
30	6/5	41.4	50.9	126.6	107.1
31	5/4	42.2	51.8	132.7	106.1
32	7/5	45.2	50.8	137.0	98.9
33	3/2	42.1	52.9	139.8	94.2
34	8/5	41.8	52.4	143.0	91.8
35	11/10	42.5	46.0	126.9	117.0
36	6/5	42.4	46.7	132.0	111.9
37	5/4	42.4	46.6	134.9	108.8
38	7/5	41.7	47.4	142.2	102.3
39	3/2	43.6	48.8	145.3	97.5
40	8/5	43.6	50.6	148.1	93.6
41	11/10	42.7	43.5	130.8	120.0
42	6/5	42.4	43.4	135.8	114.5
43	5/4	42.4	44.4	138.8	110.8
44	7/5	43.1	44.8	145.1	104.1
45	3/2	42.4	46.0	149.3	101.1
46	8/5	42.4	49.0	151.3	98.5
47	11/10	41.8	42.3	133.0	122.6
48	6/5	42.4	42.1	140.0	118.2
49	5/4	43.1	42.3	142.6	115.5
50	7/5	43.4	42.7	150.3	108.6
51	3/2	43.4	42.3	154.7	105.1

Effect of Laundering

The relationship of wale spacings to course spacings showed that both the gray and finished unlaundered fabrics were distorted. Laundering and the manual relaxation treatment eliminated the distortion, resulting in a relationship linear for the fabrics knit of each yarn (Figures 2 and 3). Figure 4 shows distortion before laundering and a linear relationship after laundering for fabrics knit of 75-den. viscose yarn with various runner ratios. The wale and course spacing relationship changed little with runner ratio. The average wale-course spacing ratio (w/p) for the acetate fabrics was 1.17 after laundering, which was slightly lower than the average ratio for the viscose tricot fabrics (1.29).

In respect to the wale-course spacing relationship, the tricot fabrics differed from the plain knit fabrics [3]. The spacings of the laundered plain knit followed a parabolic curve.

$$p^2 = a(w + b)$$

and the wale-course spacing ratio varied from 1.18 for fabrics knit of 50/1 cotton yarn to 1.28 for those knit of 12/1 cotton yarn. The ratios for the plain knit as well as for the tricot are greater than the 1.15 ratio reported by Shinn [7] for jersey fabric construction.

For all the tricot fabrics the dimensional changes that occurred in laundering were largely a geometric rearrangement. The change in length of the yarns contributed little, for it was small, usually less than 2%. Most of the change occurred in the first laundering; there was little progressive shrinkage.

In the finished fabrics that had not had the relaxation treatment the changes were usually less than 10% for the acetate but in some cases were as much

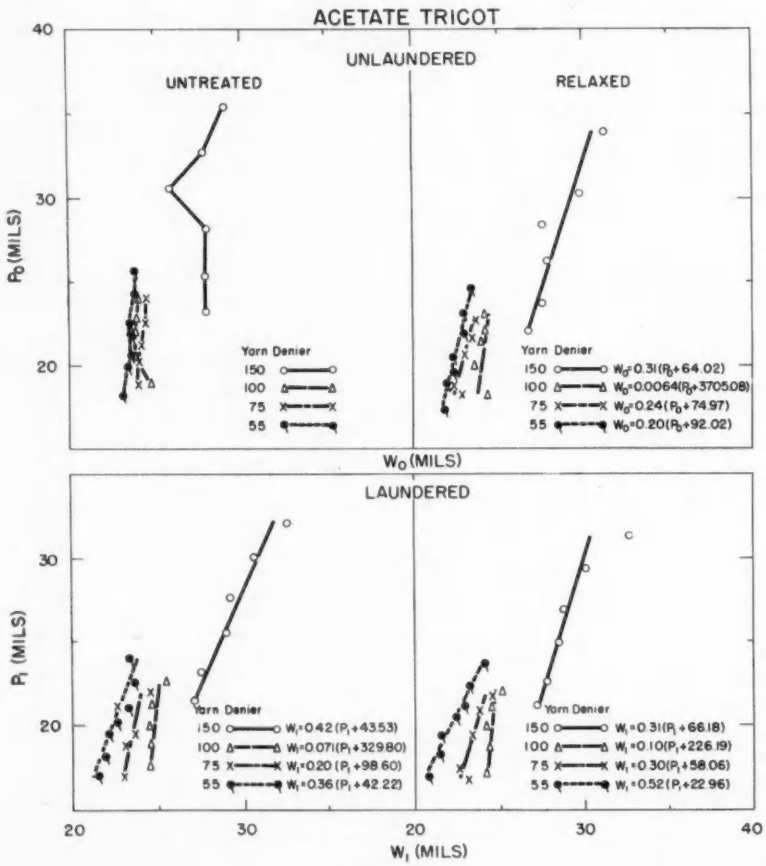

Fig. 2. The relationship of wale spacings (w) to course spacings (p) before and after five launderings and before and after the relaxation treatment of tricot fabrics knit of 150, 100, 75, and 55 den. acetate yarns with a 4/3 runner ratio. w_0 and p_0 indicate spacings before laundering; w_1 and p_1 indicate spacings after laundering.

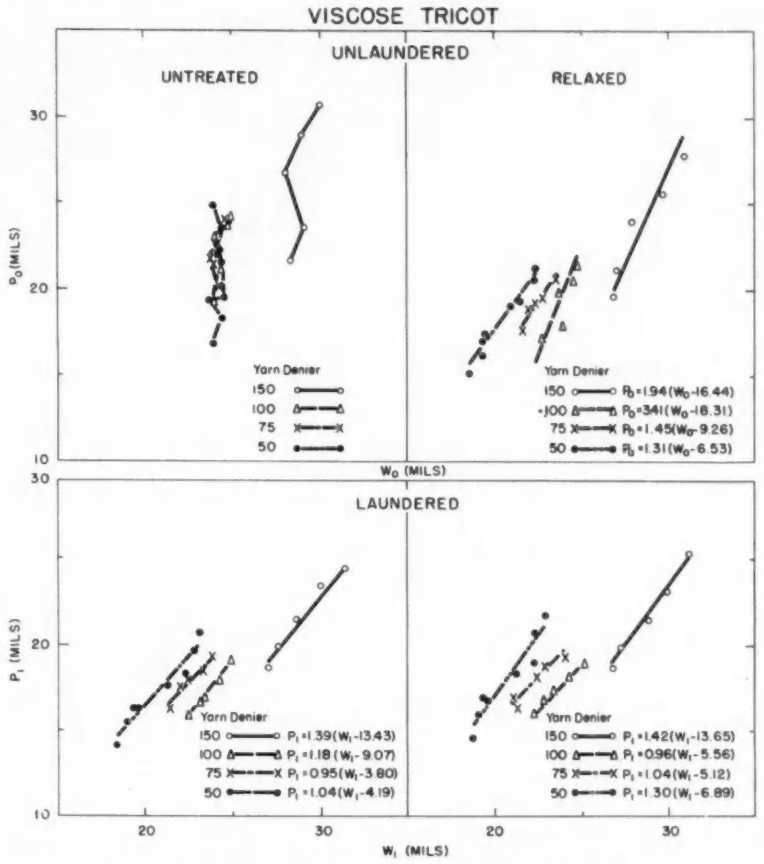

Fig. 3. The relationship of wale spacings (w) to course spacings (p) before and after five launderings and before and after the relaxation treatment of tricot fabrics knit of 150, 100, 75, and 50 den. viscose yarns with a 4/3 runner ratio. w_0 and p_0 indicate spacings before laundering; w_1 and p_1 indicate spacings after laundering.

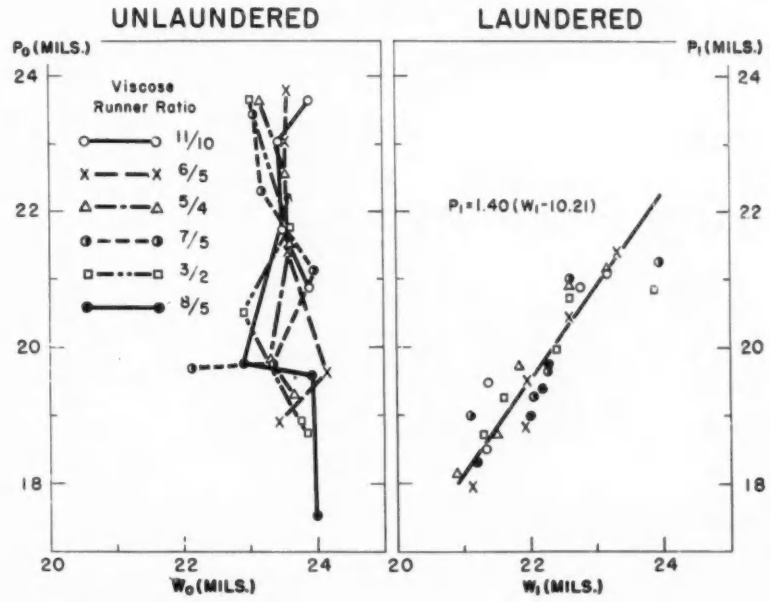

Fig. 4. The relationship of wale spacings (w) to course spacings (p) before and after five launderings of tricot fabrics knit of 75-den. viscose yarn with various runner ratios. w_0 and p_0 indicate spacings before laundering; w_1 and p_1 indicate spacings after laundering.

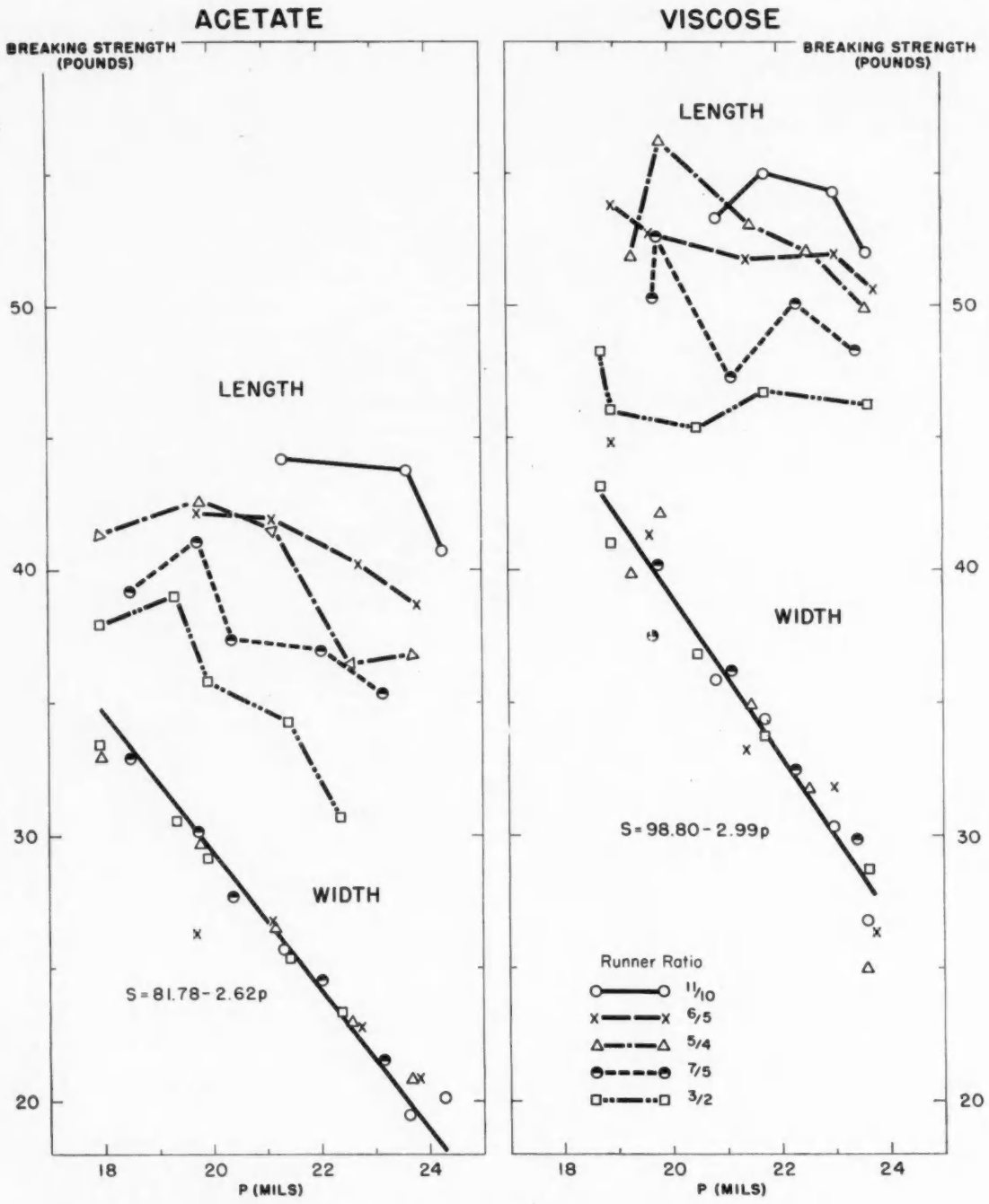

Fig. 5. The relationship of grab breaking strength (S) to course spacings (p) of tricot fabrics knit of 75-den. yarns with various runner ratios.

as 20 to 25% for the viscose. Changes were even greater in the gray fabrics, since distortion was considerable when they came from the knitting machine.

In the fabrics given the relaxation treatment, dimensional changes produced in laundering were not great; the relationship of wale and course spacings was approximately the same in the unlaundered and laundered fabrics (Figures 2 and 3). Changes were usually less than 5% for the acetate and not greater than 10% for the viscose.

Breaking Strength and Elongation

The effect of the construction of the tricot fabrics upon their breaking strength and elongation was studied. Since all of them had approximately 42 wales/in. except those knit of 150-den. yarns which had approximately 35 wales/in., no relationships could be found for wale spacings and these properties.

The length breaking strength (grab) of the fabrics decreased as the course spacings (p) increased.

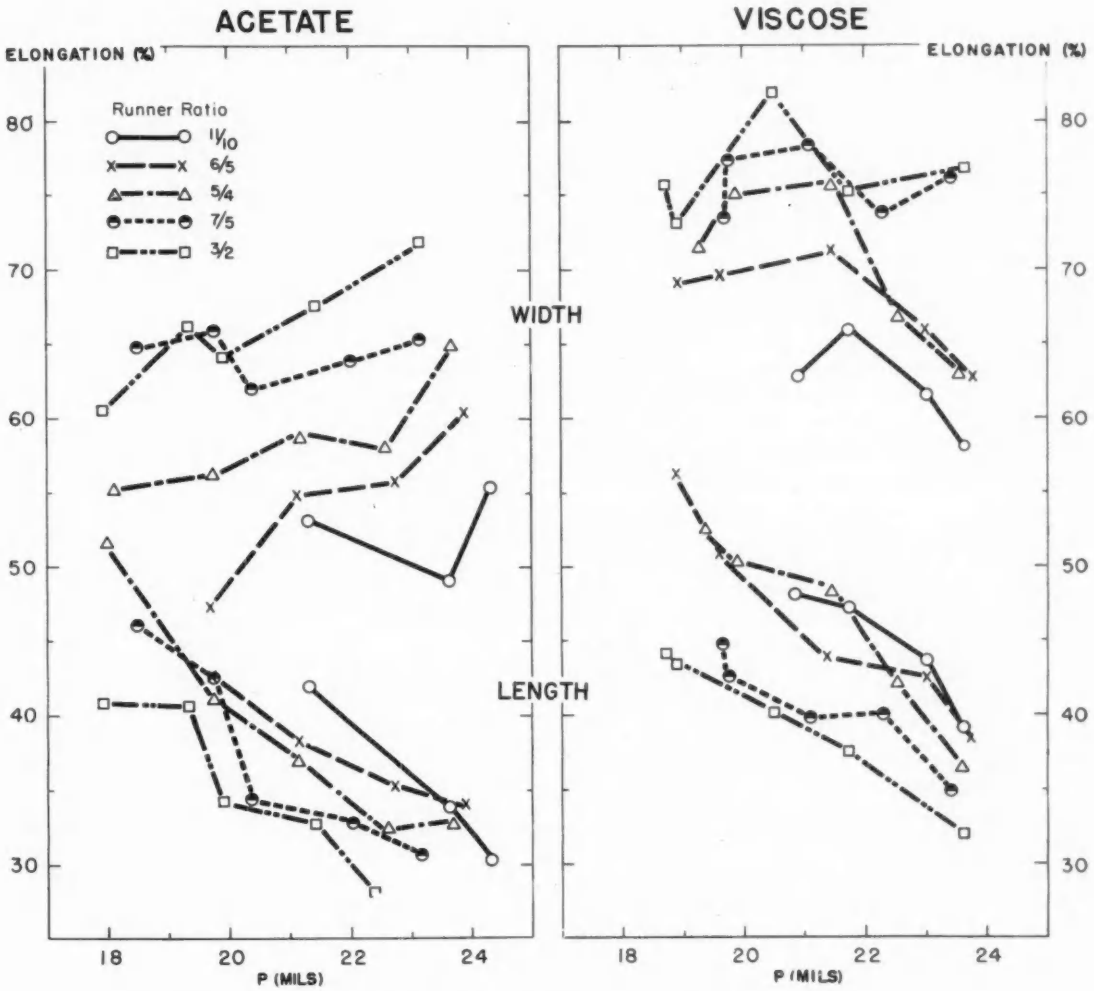

Fig. 6. The relationship of elongation to course spacings (p) of tricot fabrics knit of 75-den. yarns with various runner ratios.

The decrease was less for the viscose fabrics than for the acetate. In width breaking strength the fabrics of both fibers decreased considerably as the course spacings increased. The fabrics having the smaller runner ratios had the higher strength in the length. However, runner ratios had little influence on width strength, since the strength of fabrics of all ratios decreased at the same rate (Figure 5).

Length elongation at break decreased in all the fabrics as course spacings increased, and the fabrics having the smaller runner ratios had the higher elongation. Width elongation changed little with course spacings; in some cases there were small decreases and in others small increases as course spacings increased. The fabrics having the larger runner ratios had the greater width elongation (Figure 6).

Bursting Strength

Bursting strength also showed a marked relationship with course spacings and runner ratios. Figure 7 shows that bursting strength decreased as the course spacings increased for the fabrics knit of the four yarns of each fiber with a 4/3 runner ratio. The fabrics knit of 75-den. yarns with various runner ratios also decreased in bursting strength with an increase in course spacings. Those with the higher runner ratios (7/5, 3/2, 8/5) were considerably lower in this property than those with ratios of 11/10, 6/5, and 5/4 (Figure 8). The fabrics with the lower ratios were all about equal in bursting strength.

Stimmel reported a study [8] of acetate tricot fabrics in which the bursting strength improved slightly (33.5 to 41.5 lb.) with more courses per inch. These materials ranged in runner ratio from 1.20/1 to 1.33/1 which is a much narrower range than the 11/10 to 8/5 of the fabrics of this study. The acetate fabrics reported here varied in bursting strength from 52.5 to 69.5 lb. which indicates that a high runner ratio can decrease the strength considerably.

For the bursting strength tests, 510 specimens of the acetate and viscose fabrics (Figure 8) were used. The typical breaks (A, B, C, D, E, F, G, H) are shown in Figure 9. Of the 510 breaks

33% were perpendicular to the wales A.
32% made a 30° angle with the wales D, F, H.
12% made a 15° angle with the wales B.
8% made a 45° angle with the wales C, E.
6% made a 60° angle with the wales G.

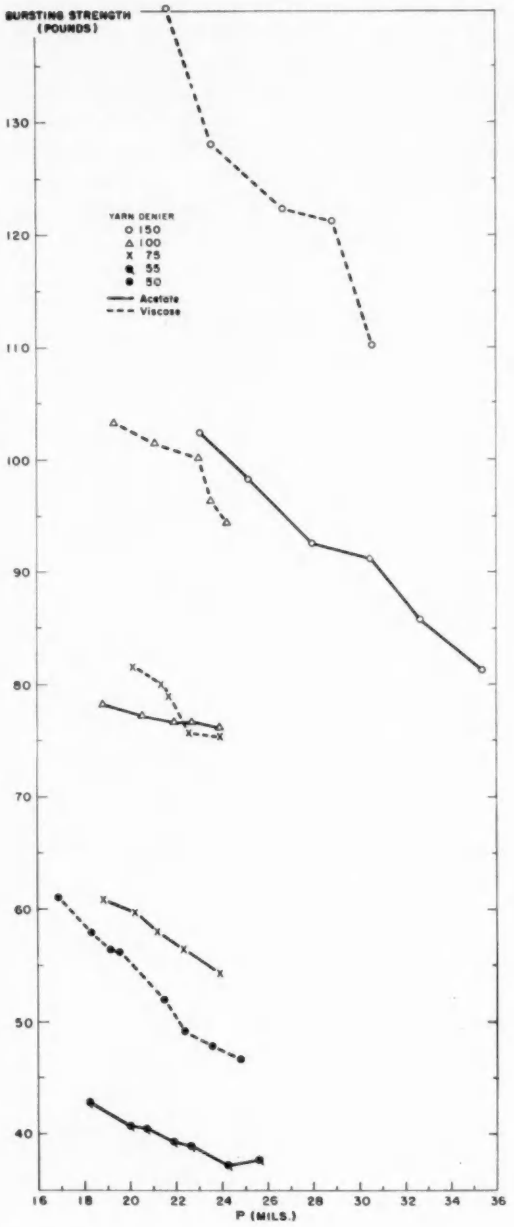

Fig. 7. The relationship of bursting strength to course spacings (p) of tricot fabrics knit of the four yarns of acetate and viscose with a 4/3 runner ratio.

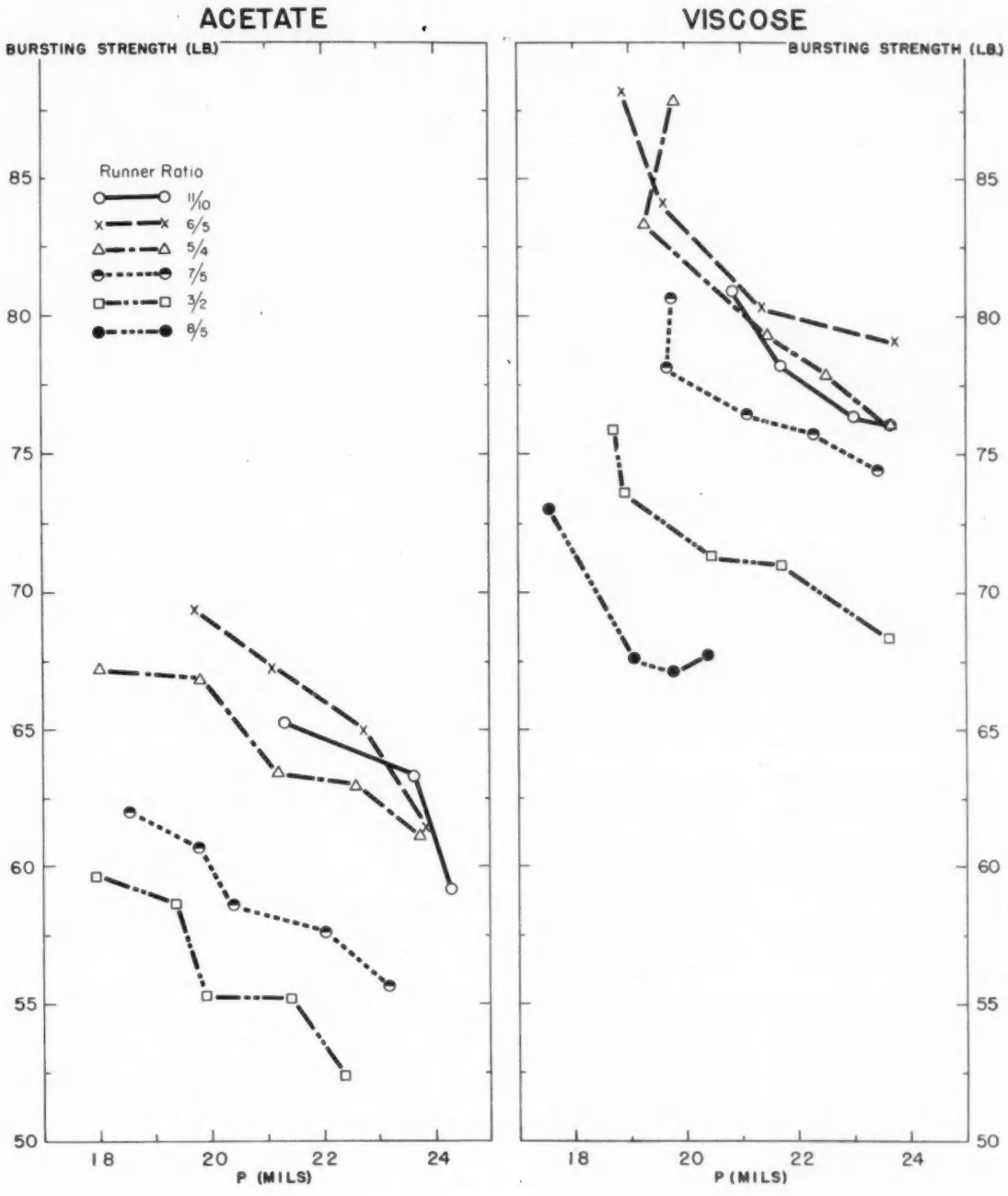

Fig. 8. The relationship of bursting strength to course spacings (p) of tricot fabrics knit of 75-den. yarns.

These typical breaks were distributed among the various ratios as follows:

Ratios 8/5 and 3/2—86% like A and remainder similar to C.

Ratio 7/5—54% like A and remainder assorted among B through F.

Ratio 5/4—9% like A and remainder assorted among C through G.

Ratio 6/5—breaks distributed from C through G.

Ratio 11/10—breaks distributed from C through H.

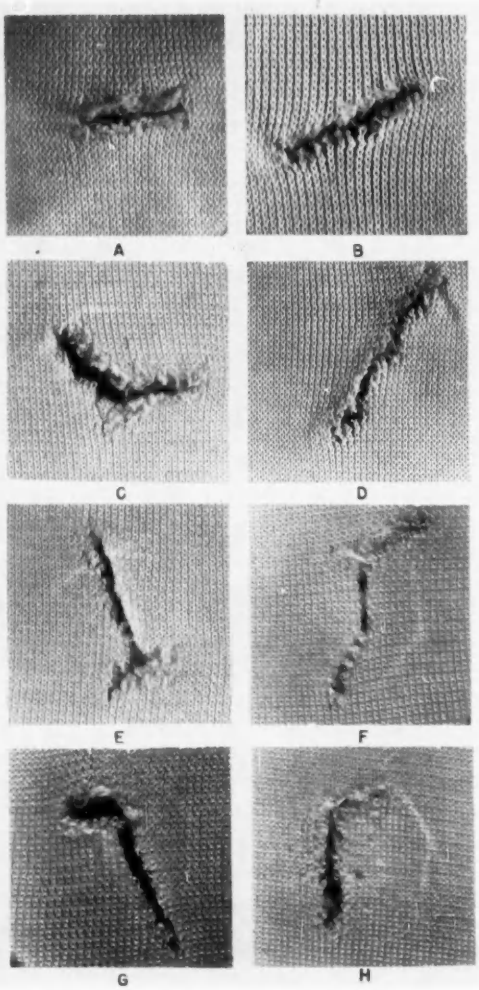

Fig. 9. Types of breaks in bursting strength tests of tricot fabrics: (A) perpendicular to wales; (H) parallel to wales; (B, C, D, E, F, G) between 15 and 60° to wales.

That is, the fabrics with a lower strength and high ratio usually broke perpendicular to the wales. As the strength increased and the runner ratio decreased, the number of breaks at an angle other than 90° increased markedly. In other words, the fabrics with the highest bursting strength broke like C, D, E, and F with no breaks perpendicular to the wales (A) or parallel to the Wales (H).

Summary

In this study of the geometry of 97 tricot fabrics knit of eight different yarns (acetate and viscose in each of four deniers) measured stitch length data showed that the length of yarn in the unit cell was: for acetate, $l_1 + l_2 = 4p + 3.5w + 11.75d$; for viscose, $l_1 + l_2 = 4p + 3.5w + 13.52d$.

The data for wale and course spacings showed that the dimensions changed considerably in laundering unless the fabrics were first given a relaxation treatment to remove distortion. For the laundered and relaxed fabrics of each of the eight yarns the relationship of wale and course spacing was linear. The average wale-course spacing ratio (w/p) for the acetate fabrics (1.17) was slightly lower than the average for the viscose fabrics (1.29).

Lengthwise the breaking strength and elongation of the fabrics decreased as course spacings increased; breaking strength and elongation increased as runner ratios decreased.

Widthwise breaking strength decreased as course spacings increased but changed little with runner ratio. On the other hand width elongation changed little with course spacings but fabrics with the higher runner ratio had the greater width elongation.

Bursting strength also decreased with an increase in course spacings. Fabrics with the higher runner ratios (7/5, 3/2, 8/5) were considerably lower in bursting strength. Those with the lower ratios (11/10, 6/5, 5/4) were about equal in strength. Fabrics with the higher bursting strength broke at angles between 30° and 45° with the wales; none with high strength broke either perpendicular or parallel to the wales.

Acknowledgment

Grateful acknowledgment is made to Elinora Johnson Williams and to Elizabeth Howard Decker for laboratory assistance.

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The Prediction of the Micronaire Value for a Bale or a Group of Bales—A Statistical Study

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Introduction

Fiber fineness as determined by the Micronaire is of increasing importance in the sale and manufacture of cotton. It is becoming common practice for mills to purchase cotton on a micronaire specification. Frequently, mills will select bales from stock so that the arithmetic mean of the micronaire reading is a particular value [5].

Those mills that concern themselves with fineness commonly identify each bale by determining the micronaire reading of

1. Each of two samples drawn from opposite sides of the bale and calculating the arithmetic mean.

2. A composite of the two samples.

The second procedure is probably the more usual because it is less time-consuming. Jennings and Lewis [3] have shown that both of these procedures will result in assigning an incorrect micronaire value to a bale if the two sides of the bale are widely different in fineness. The prediction of the micronaire value of a blend from its components must be made from the "weighted" harmonic mean rather than from the arithmetic mean. As expected, a composite whose component parts have widely different fineness must be thoroughly blended to give a precise micronaire reading. If the several cottons differ in micronaire value by no more than 1.0, the arithmetic mean is usually satisfactory. This result has been confirmed in this laboratory.

For pilot plant experiments, it is frequently desirable to know the micronaire value of a single bale. There is a variation in fineness from sample to sample within a bale, and from a knowledge of the variation of micronaire values within a bale, it is possible to show:

1. How many samples must be taken from a bale to determine the mean micronaire value of the bale with a given precision, that is, so that the mean value will not differ from the true value by more than a desired amount.

2. Or conversely, what precision is expected from a mean computed from n samples.

Frequently in industrial operations a number of bales are blended to form a homogeneous lot. The bales may be selected so that the arithmetic mean of the individual bale micronaire values has a certain value. This mean is a prediction of the micronaire value of the blend. It is of interest to know how precise these predictions are.

This paper is a report of researches designed to answer these questions. The study was made on Uplands cotton from the High Plains of Texas and

the Verne Area of Oklahoma. All bales were Strict Middling grade and $\frac{7}{8}$ or $\frac{13}{16}$ in. in staple length. No two-sided bales were observed.

The experimental procedures and results are given in the next section and are followed by a discussion of the statistical techniques used to arrive at the conclusions.

II. Experiments and Results

The Bale

Sixteen bales were selected at random from stock. The bales were opened and 12 samples were taken at random from each bale. The micronaire reading was found for each sample. The estimated arithmetic mean micronaire value $\bar{X}$, the estimated variance s^2, and estimated standard deviation s were computed for each bale (see Table I). It was found that at the 5% level of significance, the bales appeared to have the same variances (Hartley's Test, see Section III, 1). These estimated variances may be "pooled" (weighted average) to determine the variance of a bale. The pooled variance 0.0193 has 175 degrees of freedom and is considered an excellent estimate of the true variance. It may be used to predict the required number of random samples from a bale to determine the true mean micronaire value for a bale with a given precision and confidence (see Section III, 2). The calculations have been made and are recorded in Table II. For example, Table II indicates that two samples from a bale will predict a micronaire value that will not differ from the bale's true micronaire value by more than 0.2 with 95% confidence.

TABLE I. The Estimated Mean, Variance and Standard Deviation for Sixteen Bales: Twelve Samples per Bale

Bale no.	Mean	Variance	Standard deviation
	$\bar{X}$	s^2	s
1	4.425	0.018	0.134
2	4.578	0.017	0.130
3	4.729	0.044	0.210
4	4.570	0.039	0.197
5	4.671	0.026	0.161
6	4.758	0.015	0.122
7	5.250	0.006	0.077
8	4.858	0.012	0.109
9	4.817	0.021	0.145
10	4.025	0.017	0.130
11	4.783	0.009	0.095
12	4.521	0.044	0.209
13	4.483	0.007	0.084
14	4.583	0.007	0.084
15	3.758	0.017	0.130
16	5.237	0.009	0.095

TABLE II. The Number of Samples Required to Predict the Mean Micronaire Value of a Bale with a Given Precision

$s_p = 0.139$

Precision	Number* of samples required at various confidences 90%	95%	99%
0.1	6(5.6)	8(7.7)	18(17.4)
0.2	2(1.4)	2(1.9)	5 (4.3)
0.3	1(0.6)	1(0.9)	2 (1.9)

* Values in parentheses are the number of samples calculated to the nearest tenth. Rounding off to the next highest number increases the confidence or improves the precision of the production.

Group of Bales

Many mills find it desirable to blend a group of bales to a particular micronaire value. Their practice is to determine the micronaire value of each bale by one of the sampling procedures previously described. Bales to be blended are selected so that the arithmetic mean of the individual bales is the desired value [5]. *A priori* there is no reason to expect that this practice will not on the average give an accurate prediction, but the precision of such predictions is of interest.

The micronaire value predicted for a bale based on one micronaire determination of a composite of two samples taken from the bale was compared with the prediction obtained by one determination on a well-blended composite of six random samples taken from the bale. The six-sample composite X_6 is likely to be more representative of the true micronaire value of the bale than the two-sample composite X_2. In Table III are recorded the frequency distribution of the absolute differences $|X_2 - X_6|$ of the predictions of these two sampling procedures.

The prediction of the micronaire value for a blend of N bales based on a practical sample, a composite of two per bale was compared with the prediction of a more extensive sampling procedure, a composite of six per bale. The standard deviation of the differences was found to be 0.393 and was used to calculate the predictions in Table IV (see Section III, 3). The figures in the right-hand column indicate the maximum difference at 95%

TABLE III. Frequency Distribution of Absolute Differences in Predicted Mean Micronaire Values for Individual Bales Sampled in Two Ways

Absolute difference $\lvert X_2 - X_6 \rvert$	Number of bales
1.4	1
1.1	1
1.0	2
0.8	1
0.7	1
0.5	2
0.4	6
0.3	11
0.2	14
0.1	12
0.0	4
Total	55

TABLE IV. The Calculated Maximum Differences $\lvert \bar{X}_2 - \bar{X}_6 \rvert$ between the Predicted Micronaire Values for *N* Bales Sampled in Two Ways

(95% Confidence)

No. of bales	Maximum difference $\lvert \bar{X}_2 - \bar{X} \rvert_6$
2	0.56
6	0.32
8	0.28
10	0.25
11	0.24
20	0.18
26	0.15
30	0.14
40	0.12
100	0.08

confidence between the predictions for N blended bales when the two sampling procedures are used. For example, if ten bales are blended, in only five out of 100 cases will the predictions of the practical sampling procedure and the more extensive procedure differ by more than 0.25.

The predictions of precision as a function of the number of bales blended are given in Table IV. These predictions were checked experimentally. Fourteen lots each composed of 11 bales were processed. One micronaire value was determined on a composite of two unblended samples from each bale (X_{i2}). The "predicted" value X_2 for the blend of 11 bales was determined $\bar{X}_2 = \frac{1}{11}\sum_{i=0}^{11} X_{i2}$. The 11 bales in each lot were opened simultaneously by introducing a layer of each into the opening equipment. Samples were taken at 10-min. intervals after the cotton had passed through the lint cleaners. A total of 15 samples were taken and blended on the U.S.D.A. fiber blender. Five micronaire determinations were made on the blended composite, and the estimated mean $\bar{X}_L$ was determined. The difference $\bar{X}_2 - \bar{X}_L$ was found for the 14 lots. The frequency distribution of the differences is shown in Table V. Only one of 14 lots showed a difference larger than 0.2. According to the data in Table IV for 11 bale lots, only 5% of the lots should show differences greater than 0.24. The agreement is reasonable.

TABLE V. Observed Frequency Distribution of Differences between the Predicted and the Estimated Mean Micronaire Value for Lots of Eleven Bales

Difference $\lvert \bar{X}_2 - \bar{X}_L \rvert$	Frequency
0.3	1
0.2	2
0.1	7
0.0	4
Total	14

III. Statistical Analysis

1. *Hartley's Test* [4]. A test of variances to determine if it is likely that all of the bales come from one population.

2. Number of samples required to predict the true mean μ with a given precision (Table II). The number of samples N is determined from the ratio [1].

$$\frac{\bar{X} - \mu}{\sigma N^{\frac{1}{2}}} = t$$

where μ is the true mean, $\bar{X}$ is the estimated mean, and $\bar{X} - \mu$ is the precision. This ratio can be used only when the true standard deviation of the population is known. By virtue of the large number of degrees of freedom on which the estimate of the standard deviation is based, it is statistically reasonable to assume that the estimate is the true standard deviation. The statistic t is obtained from tables of Student t, and the value chosen determines the confidence of the prediction.

A similar ratio [1]

$$\frac{\bar{X}_1 - \bar{X}_2}{\sigma\sqrt{\frac{1}{N_1} - \frac{1}{N_2}}} = t$$

makes it possible to determine the number of samples required from each bale to ensure that the two bales have mean micronaire values that are not different by more than $\bar{X}_1 - \bar{X}_2$.

It can be shown that $N_1 + N_2$ will be a minimum when $N_1 = N_2$. For this particular condition, *each* bale must be sampled twice the number of times indicated in Table II for the appropriate difference.

3. The maximum differences in Table IV were calculated from the *t*-distribution [2].

$$|\bar{X}_2 - \bar{X}_6| = t \times \frac{s}{\sqrt{N}}$$

where $\bar{X}_2$ and $\bar{X}_6$ are the predicted averages for N bales calculated from the values for each bale based on one micronaire determination on composites of two and six samples per bale, respectively. The estimated standard deviation s is 0.393 and t was taken from Student t tables for 95% confidence and 55 degrees of freedom.

IV. Conclusions

1. The within bale variances of micronaire value in the bales of cotton studied which were grown in the High Plains of Texas and Oklahoma are statistically homogeneous. It should be pointed out, however, that these bales may or may not be representative of all American Upland cottons, nor even, in fact, of all cottons from the areas in which the samples were grown.

2. To predict precisely the true mean ($\mu \pm 0.1$) micronaire value of one bale with 95% confidence, eight random samples are required (Table II).

3. The usual practice of predicting the average micronaire value of a group of bales from one micronaire determination on a composite of two samples from the outer sides of the bale gives a precise ($\mu \pm 0.2$) prediction when 20 or more bales are blended (Table IV). The precision of the prediction when less than 20 bales are blended can be improved if the micronaire value of two samples from each bale is determined.

V. Acknowledgment

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